nature portfolio

Peer Review File

Extraordinary Phase Transition Revealed in a van der Waals Antiferromagnet

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Guo et al present a detailed study on the exfoliatable antiferromagnet CrSBr using second harmonic generation optical spectroscopy to probe the symmetry-breaking of the surface layers. The authors also use density functional theory to calculate the difference in interaction strength between monolayer and bulk CrSBr, showing that the mean field exchange is stronger in the monolayer limit. They interpret this as "extraordinary" phase transition wherein the bulk orders at a lower temperature than the surface.

Although the experiments and analysis are of very good quality, I have several concerns about the authors interpretation.

Firstly, the authors need to distinguish their results from mere two-dimensional order. At this point, several studies (notably Refs. 21, 22, 23, and 24) have proposed that CrSBr has an intermediate "two-dimensional ordered" or "intralayer order" phase above the bulk TN, wherein every plane of Cr atoms has symmetry-breaking magnetic order, but the planes themselves are uncorrelated. What the authors have not shown is that their measurements are not merely detecting this "intralayer order". Under this scenario, there is no substantial difference between surface and bulk in the onset of symmetry-breaking spin correlations, and what the authors are detecting with SHG is the same (or similar to) what they would see if they were probing the interior of the sample. In that scenario, there would be no "extraordinary" phase transition. I see no real discussion of this possibility in the paper, but the authors need to rule it out if they wish to make a separated surface-bulk transition their central result.

Second, the crux of the "extraordinary" phase transition is their observation of a Neel temperature. Besides questions about the error bars on this value (see below), there are already conflicting reports of TN in the literature, even from the same probes (e.g., neutron diffraction). Readers will therefore harbor some skepticism that (a) the observation that TN=140K is totally new, and (b) it should be taken at face value. Especially in van der Waals materials, the Neel temperature can be affected by all sorts of factors besides the probe itself (including how the sample was handled between measurements, c.f. RuCl3 http://dx.doi.org/10.1103/PhysRevB.93.134423).

Minor comments:

1.

p. 2: “The transition establishing the bulk order, while the surface one is already present,” <-- this is confusing wording. Consider rewording to “…while the surface is already ordered,”

2.

p. 3: “CrSBr batch exhibits a clear order-parameter-like upturn at 140 K (Fig. 2e), a new temperature scale for 3D CrSBr crystals, not detected by any probes for bulk properties…” <-- It is perhaps a stretch to claim this is a new temperature scale. Given the previously reported TN=140K result for the bilayer (ref. 21), it seems that the authors here are simply stating that the energy scale of the surface is equal to that of a bilayer. Furthermore, anomalies at this temperature were observed in bulk magnetoresistance (ref. 24), so this temperature scale has been reported and discussed before for CrSBr.

3.

Maybe I missed it, but do the authors report the thickness of the sample they measured?

4.

Was the order parameter curve collected on heating or cooling, and what was the heating rate? When there are conflicting reports of TN, differences in heating/cooling rate are often the culprit, so this is important to report.

5.

The distinguishing of different domains via SHG is very clever work.

6.

“Note that D is expected to be about the same in a single monolayer and in the bulk.” <-- Why? Naively, one would expect the additional broken symmetries on the surface to allow for more asymmetric exchange there than in the bulk (c.f. Moriya’s rules).

7.

The TN reported in the paper and fit in Fig. 2 panel (d) needs error bars to be compelling. The first data point below 140K is not outside error bars of the data points immediately to the right. Therefore it is statistically unjustified to treat it as the first point in the order parameter curve. This is especially important because the reports of finite intralayer ferromagnetism above TN would mean that one would see an upturn in the order parameter above TN, making it tricky to precisely nail down where the upturn begins. The authors should provide a fitted TN and \Beta exponent to compare with other studies, most notably Refs. 21, 23, and 26.

8.

Fig. 2 caption: “unreported onset at 140 K”. Again, saying this temperature is “unreported” is a step too far. It was reported in few-layer compounds and in powder neutron diffraction and in magnetoresistance.

Summary:

The main result is that the Neel temperature from SHG is greater than the Neel temperature from the bulk. However, there is already conflicting accounts of the Neel temperature in neutron diffraction (Ref. 23 vs. 26), so if I play the skeptic, I would say that this could be a discrepancy in sample quality, experimental protocol, or some other artifact. Furthermore, the authors should explain more the why they believe they are not simply observing the “intralayer correlations” discussed by others.

That said, the authors have done a very good job in their data collection and treatment, and the DFT results are quite compelling. Given appropriate revisions, this paper would be suitable for publication in Nature Communications.

Reviewer #2 (Remarks to the Author):

I reviewed the paper by Guo et al entitled "“Extraordinary” Phase Transition Revealed in a van der Waals Antiferromagnet", which include SHG experiments, HAADF-STEM, and ab initio simulations on the different critical temperatures observed in CrSBr at the surface and at the inner bulk part of this compound. The paper discuss the possibility to stabilise different phase transitions at the bulk and surface as measuring the surface-sensitivity dipole moments. I'd have a few comments on this manuscript that would restrict its acceptance. I would recommend a full revisions of this manuscript, and send it to a more technical journal.

1) It is well known in the field that different samples (from different groups) can give different transition temperatures since we haven't achieved any standard guidelines or receipts that would allow the control of defects, step-edges, grain-boundaries, surface roughness, etc. 2D magnetic materials are still far way from more standard protocols in place for other materials, e.g. graphene,

TMDs, h-BN, etc. So, further measurements on different samples, produced in different way would be helpful to sort the variations in temperature observed.

2) It is really not convincing the way it is separated contributions from inner bulk and surface. I understand the difficulties to try to deconvolutionate the signal, which even so, it would not be clear. I looked for some information of any penetration depths in the measurements, or some plot showing the SHG vs. penetration depth, but nothing is included. Without knowing this information, not much can say about different temperatures at the surface and inner bulk. Moreover, penetration depths would only provide part of the solution since it could also be the case that the layers are only probed until certain thickness, and the rest not. So, it doesn't mean that the surface might have a different transition temperature, relative to bulk, but only a few layers would be considered. There is no simple solution for this problem though.

3) Following up from my previous comments, normally the best way to try to solve this uncertainty between bulk and surface is to have materials with different crystal symmetries; or the same one, but in different crystal phase. I can see that the authors characterised the crystals (Figure 2), which seems in good crystallinity across the thickness. So, there is not simple way to separate contributions from the surface from those in the bulk.

4) About the SHG signal at 80 K (Fig 3c,3d), domain A/B, which translate in Figure 4b, both situations are possible. However, it does not mean that a phase transition is taking place differently at the surface and inner bulk. My impression looking at this dataset is that the authors are measuring how two possible magnetic coupling may exist at the same temperature, which indicates the meta-magnetic character of CrSBr. Other 2D magnets don't show this, but it doesn't mean different phase transitions at different parts of the crystal though.

5) The theoretical part is very simple with several limitations on the description of the interactions, system, etc. In particular, the spin Hamiltonian included at the end of the manuscript (no number referring to it in the text!) corresponds to only exchange interactions, without any anisotropy terms, dipolar interactions, DMI, etc. Indeed, CrSBr has a biaxial magnetic anisotropy which needs to be taken into account to produce accurate results.

6) Moreover, the equation for T_N referred to 'Mermin-Wagner formula', cited Ref.44, has nothing to do with the Mermin-Wagner's PRL paper in 1966, but rather by the S Todo's lab in 2005. Proper acknowledgment needs to be included. So, I'd suggest the authors to refer to Ref.44 , and remove the term 'Mermin-Wagner' throughout the paper, which nothing has to do with that.

7) Following up from my previous comments, the equation for T_N is a mean-field based equation which has several limitations on the consideration of exchange interactions, thermal effects, etc. In order to be convincing proper micro-magnetic or atomistic simulations would need to be undertaken at different thickness, system sizes, etc. in order to elucidate any dependence of the transitions at the surface and inner bulk. The variation of T_CW, J_1,2,3 with the Hubbard-U parameter is really not convincing. This seems very adjusted to the system size to give the corresponding results, which seems artificial. The Hubbard-U might be dependent on the thickness of the system (e.g. 1L, 2L, ..) relative to bulk. However, once it is calculated for that particular thickness (via linear response, or Monte Carlo, etc.), and it should be constant, and not anymore tunable.

8) Thermal fluctuations might happen at the surface as it is pointed out (page 6), but they tend to thermalise and consequently dying out with time. If the system is not in equilibrium initially, it would be very hard to measure any property thermodynamically speaking. So, this argument to explain the increase in the magnetic onset temperature at the surface seems not the case here.

9) The paper is very confusing in the way the different types of potential transitions occurred at finite system, the first paragraph would need a full re-writing, and the definitions reviewed.

Reviewer #1 (Remarks to the Author):

Guo et al present a detailed study on the exfoliatable antiferromagnet CrSBr using second harmonic generation optical spectroscopy to probe the symmetry-breaking of the surface layers. The authors also use density functional theory to calculate the difference in interaction strength between monolayer and bulk CrSBr, showing that the mean field exchange is stronger in the monolayer limit. They interpret this as “extraordinary” phase transition wherein the bulk orders at a lower temperature than the surface. Although the experiments and analysis are of very good quality, I have several concerns about the authors interpretation.

We thank Reviewer #1 for carefully reading our manuscript and assessing our work positively. Below, we provide a point-to-point response to the reviewer’s questions.

Firstly, the authors need to distinguish their results from mere two-dimensional order. At this point, several studies (notably Refs. 21, 22, 23, and 24) have proposed that CrSBr has an intermediate “two-dimensional ordered” or “intralayer order” phase above the bulk T_N, wherein every plane of Cr atoms has symmetry-breaking magnetic order, but the planes themselves are uncorrelated. What the authors have not shown is that their measurements are not merely detecting this “intralayer order”. Under this scenario, there is no substantial difference between surface and bulk in the onset of symmetry-breaking spin correlations, and what the authors are detecting with SHG is the same (or similar to) what they would see if they were probing the interior of the sample. In that scenario, there would be no “extraordinary” phase transition. I see no real discussion of this possibility in the paper, but the authors need to rule it out if they wish to make a separated surface-bulk transition as their central result.

We thank Reviewer #1 for this question on differentiating between 1) the *c*-axis incoherent intermediate “intralayer order” reported in the literature and 2) the surface layered AFM order reported in our current work.

Please let us start by summarizing the key temperature scales that we see in our temperature-dependent RA SHG measurements (i.e., Figure 5 of the main text): T^{**} = 155K that we assign to a cross-over temperature scale, where we observe a clear increase in the bulk EQ SHG signal (Figure 5c), T_s = 140K that we attribute to the surface AFM order onset, where we detect an order parameter-like onset in the surface ED SHG signal (Figure 5b), and T_N = 132K that we associate with the bulk AFM order onset, where we capture a kink both in the surface ED SHG (Figure 5b) signal and the bulk EQ SHG signal (Figure 5c).

We then compare to the *c*-axis incoherent intermediate “intralayer order” reported in the literature and can successfully distinguish our surface AFM order onset at T_s = 140K from this previously reported “intralayer order”, based on the two key differences below.

1) **Temperature scale difference:** The temperature scale for the reported intermediate “intralayer order” varies between 155K and 170K in the literature (i.e., ~160 K from *Nano Letters 2021, 21, 3511-3517* and *Adv. Sci. 2022, 9, 2202467*, ~155 K from *ACS Nano 2022, 16, 15917−15926*, and ~170 K from *Nature Materials 2022, 21, 754–760*). This temperature scale is substantially higher than our surface AFM onset temperature of T_s = 140K, but coincide with our observed cross-over temperature scale of T^{**} = 155 K (please see below for the reason of our assignment of a “cross-over” to it instead of a phase transition at T^{**} = 155 K). Therefore, we are confident that our surface AFM order is different from the reported “intralayer order” in the literature.

2) **Symmetry difference:** The symmetry point group for the reported bulk “intralayer order” is *mmm1’* due to the *c*-axis incoherence. With such a point group, we cannot explain the mirror and C_2 symmetry breaking below 140K (Figure 3 of the main text). To account for these broken symmetries, we had to choose *m’m2’* point group for the order onset at 140K, which is fully consistent with a surface layered AFM order point group. Because of this, we further believe that our observation at 140K should be associated with the surface AFM order and distinct from the reported bulk “intralayer order”.

Inspired by this question from Reviewer #1, we further performed thickness dependent RA SHG at low temperature (i.e., 80K), to **confirm** the surface ED SHG origin from the surface AFM order. We investigated three different thickness, 160nm, 450nm, and 7500nm (7.5 μm) that are quantified by the atomic force microscopy measurements. In Figure R1, we show their RA SHG patterns in the S_{in}-S_{out} channel and their decomposition into the bulk EQ and surface ED contributions. We can clearly see that:

a) As the thickness increases, the surface ED SHG contribution stays nearly the same. This is consistent with its surface nature.
b) In contrast, when the thickness increases, the bulk EQ SHG contribution also increases, which is consistent with its bulk nature. From the trend, we can also roughly estimate our light penetration depth is slightly deeper than 450nm.

With the confirmation of the surface origin of SHG that onsets at T_s = 140K and its symmetry properties, we are confident about our assignment of the surface layered AFM order that is distinct from the bulk *c*-axis incoherent “intralayer order”.

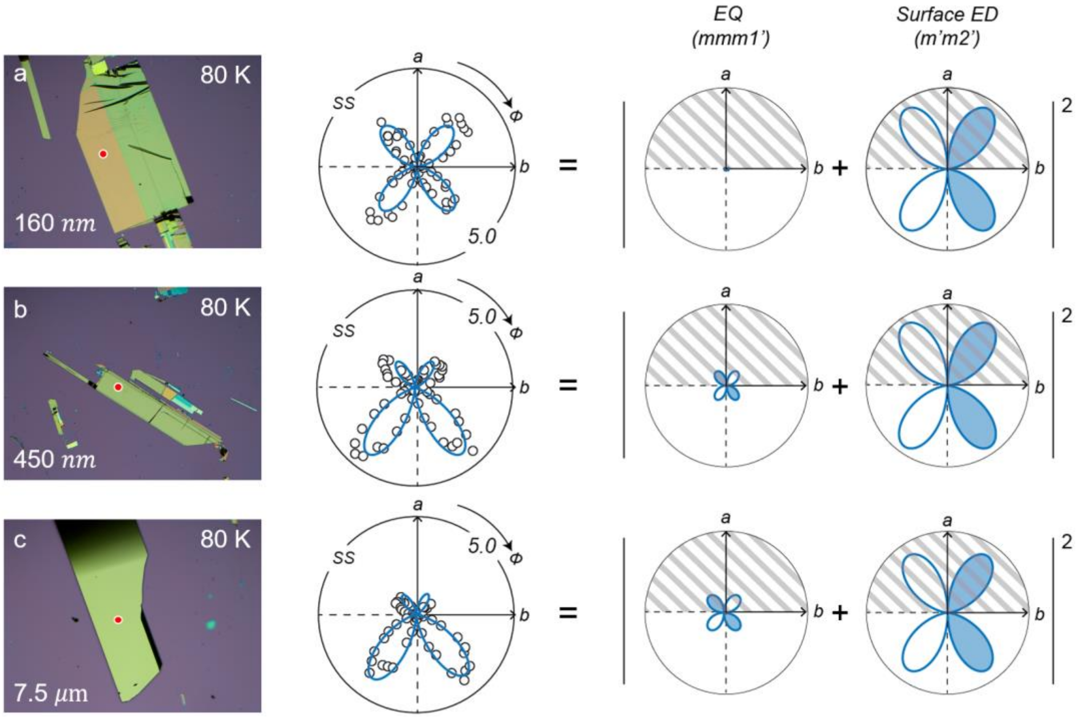

Figure R1 | Thickness dependent SHG RA. Optical image, bulk EQ and surface ED SHG contributions and their interference for samples with thickness **a**. 160 nm **b**. 450 nm and **c**. 7.5 μm. All the patterns are measured at 80 K. Red dots in the optical images indicate the location for SHG measurements.

We also take the opportunity to explain our assignment of T^{**} = 155K to be a cross-over temperature scale. In the earlier works by others [*Nano Letters 2021, 21, 3511-3517*, *Adv. Sci. 2022, 9, 2202467* and *Nature Materials 2022, 21, 754–760*] and ourselves [*ACS Nano 2022, 16, 15917−15926*], this temperature scale around 155K has been observed and is attributed to the emergence of an intermediate "intralayer order" without the *c*-axis coherence. However, upon the careful RA SHG study of this current work, we realize that we may need to provide a revised interpretation for the magnetic behavior across 155K. **Our revised interpretation** for T^{**} = 155K is a temperature scale, below which the spin forms fluctuating, short-ranged patches within and between *ab*-planes for the entire bulk. Within each patch, the spins on average align along the *b*-axis direction (Figure R2a). Then, below T_s = 140K, the surface layers order in the layered AFM state whereas the deeper bulk remains in the fluctuating, short-ranged form (Figure R2b). And finally, below T_N = 132K, the entire sample enters the layered AFM state (Figure R2c). The reasons for this revised assignment are listed as follows:

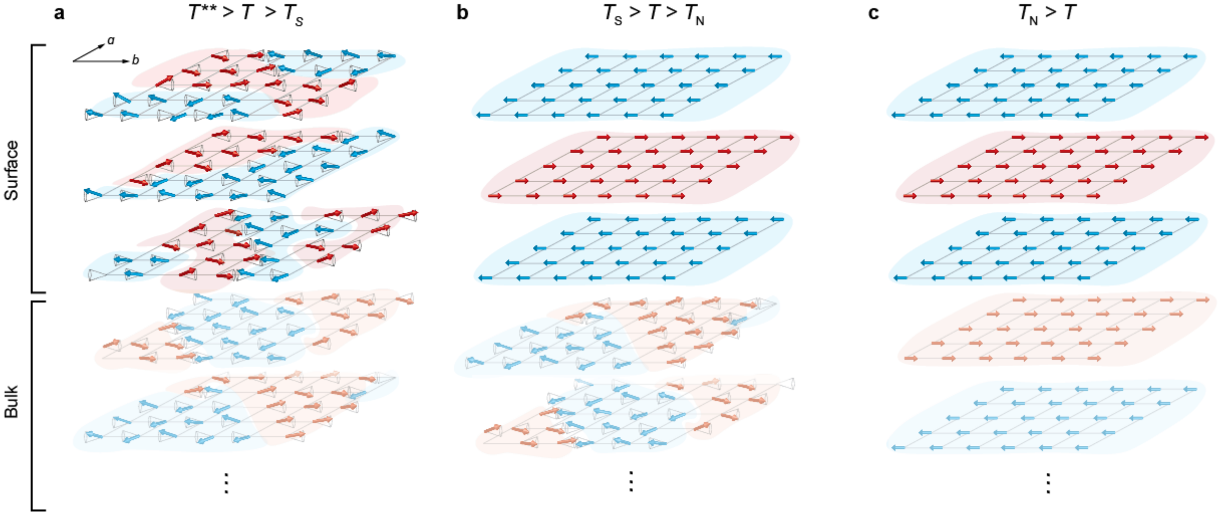

Figure R2 | Proposed spin texture at various temperatures. **a**. At $T^{**} > T > T_s$ the whole sample develops a multi-patch state with short-range correlations. **b**. At $T_s > T > T_N$, the surface develops layered AFM order, whereas the bulk still only has short-range correlations. **c**. $T < T_N$, a long-range layered AFM order is developed across the sample.

1) We observed both T^{**} = 155K and T_S = 140K, in addition to T_N = 132K, in the temperature dependent RA SHG data. If the spins form the ferromagnetic long-range order within the ab-plane below T^{**} = 155K, we can ask what changes in RA SHG would be upon the formation of this state. From the symmetry perspective, the surface magnetic point group of this *c*-axis incoherent magnetic state is *m'm2'*, and the bulk magnetic point group is *mmm1'*. Due to the in-plane long-range order, we would anticipate the surface ED contribution and the bulk EQ contribution to RA SHG right below T^{**} = 155K. In addition, due to the *c*-axis incoherence, its surface magnetic state has 2^N options, where N is the layer number for surface magnetism, and therefore we would expect 2^N degenerate domain states. However, right below T^{**} = 155K (above T_S = 140K), we don't observe surface ED SHG in our data and only find one type of RA SHG between T^{**} and T_S. This distinction between our expectation of RA SHG for the *c*-axis incoherent state and the observed RA SHG between T^{**} and T_S motivates us to consider a different possibility of the magnetic state between T^{**} and T_S.

2) At the same time, our proposed picture of fluctuating, short-ranged patches with an average spin alignment along the *b*-axis inside patches is consistent with our experimental data. As there is no global symmetry breaking either at the surface or inside the bulk, we don't observe changes in RA SHG patterns across T^{**}. But because there is an average effect to make the *b*-axis slightly different from the *a*-axis throughout the sample, we do observe in the bulk EQ SHG that the susceptibility tensor element amplitudes change.
3) After careful thinking and extensive discussions, we find the transition from the *c*-axis incoherent "intralayer order" to the layered AFM order is unlikely to happen at T_N = 132K for bulk CrSBr. Between these two states, the energy gain is in the order of $\Delta E \sim nNJ$, where J is the interlayer AFM exchange coupling, n is the number of interlayer bond per two neighboring layers, and N is the number of layers for a bulk sample. And between these two states, the entropy reduction is $\Delta S \sim k_B N \ln 2$, as the number of possible states reduces from 2^N to 2. A thermodynamic phase transition can happen when $\Delta E = T_c \Delta S$, leading to a critical temperature of $T_c = \frac{nJ}{k_B}$. For the intralayer long range orders, $n \to \infty$ and therefore $T_c \to \infty$, rather than the finite temperature of T_N = 132K. Therefore, it is unlikely that the bulk magnetic state has the *c*-axis incoherent "intralayer order" below 155K.

With these considerations, we assign the observed temperature scale of T^{**} = 155K to be a cross-over temperature scale for the system to enter a state with fluctuating, short-ranged patches of spins that on average align with the *b*-axis within individual patches.

In summary, our temperature dependent RA SHG indeed captures both T^{**} = 155K and T_s = 140K, in addition to T_N = 132K. We assign T_s = 140K to be the surface layered AFM order temperature due to its distinct temperature and symmetries from the intermediate "intralayer order" reported in literature. We revise the interpretation of T^{**} = 155K, from the onset of the intermediate "intralayer order" in the literature, to a cross-over into a fluctuating, short-ranged spin state.

Actions taken: We have made the following changes to address this question:

1) We confirmed the surface origin of the SHG signal onset below T_s = 140K through the additional thickness dependent SHG measurements. We added the thickness dependence in the Supplementary Materials Section 7, and we added in Lines 144-147 of the main text.

> "Moreover, the thickness dependent RA SHG measurements below T_N show an increasing trend of the EQ SHG contribution, but a constant level of the ED SHG contribution with increasing sample thickness, which is consistent with their assigned bulk and surface origins, respectively (see Supplementary Section 7)."

2) We discussed in-depth the three temperature scales found in our experiment, T^{**} = 155K, T_S = 140K, and T_N = 132K and explained the reasons for their assignments to a cross-over, surface AFM order, and bulk AFM order temperatures, respectively. We revised the main text and figures to convey the message.
   - in Lines 184-186 of the main text by adding
     "Three important temperature scales are captured in the temperature dependence of ED and EQ contributions, T^{**} = 155 K, T_S = 140 K, and T_N = 132 K that are discussed in-depth below (see Supplementary Materials Section 9 for data from another sample)."
   - in Lines 197 – 218 of the main text by adding

> “To understand these three observed temperature scales, we compare them with the literature reported ones for CrSBr of bulk, powder, and film forms. First, our bulk AFM order onset temperature, $T_N = 132$ K, is consistent with that of bulk CrSBr single crystals measured by single crystal neutron diffraction, μSR, heat capacity, and magnetic susceptibility[20-27]. Second, our surface AFM order onset temperature, $T_S = 140 \pm 0.2$ K, coincides with the magnetic critical temperature reported for powder CrSBr measured with powder neutron diffraction[26] and bilayer CrSBr with SHG[21]. For powder CrSBr, it is true that the surface to bulk ratio significantly increases from that for single crystal CrSBr, and thus it is likely that the surface magnetism is detected by the powder neutron diffraction. For bilayer CrSBr, it resembles the surface magnetism in 3D CrSBr in the way that they both miss neighboring layers on one side. Therefore, our detection of $T_S = 140 \pm 0.2$ K for the surface magnetic order in 3D CrSBr offers potential explanations for the variation in the magnetic critical temperature of CrSBr. Finally, the temperature scale of $T^{**} = 155$ K was previously assigned to the onset of an intermediate *c*-axis incoherent ferromagnetic state, where the spins align ferromagnetically within individual *ab*-planes but randomly between adjacent *ab*-planes throughout the bulk of 3D CrSBr[21-24]. However, it is thermodynamically unlikely to achieve a phase transition from this intermediate order without *c*-axis coherence to the layered AFM order at $T_N = 132$K for 3D bulk CrSBr, because the energy change scales with volume but the entropy change is proportional to the thickness, leading to a divergent (infinite) critical temperature for this phase transition. As a result, we revise the interpretation of $T^{**} = 155$ K to be a cross-over temperature scale below which the spins form fluctuating, short-ranged patches both within and between *ab*-planes (Fig. 5e). Within individual patches, the spins on average align more along the *b*-axis, making the *b*-axis more different from the *a*-axis and thus resulting the EQ SHG change across T^{**} (see Supplementary Materials Section 11 for detailed explanations).

- in Lines 219 – 223 of the main text by adding
  “Our experimental findings are summarized by the sketches in Figs. 5e – 5g. At $T^{**} > T > T_S$, 3D CrSBr undergoes a cross-over into fluctuating, short-range magnetic patches with the spins on average aligning more along the *b*-axis. At $T_S > T > T_N$, the surface of 3D CrSBr experiences a surface magnetic phase transition into the surface layer AFM order, whereas the deeper bulk remains the same as at $T^{**} > T > T_S$. Finally at $T < T_N$, the entire 3D CrSBr enters the layered AFM ordered phase.”
- in Figure 5 by adding illustrations of magnetic states over the three temperature windows: $T^{**} > T > T_S$, $T_S > T > T_N$, and $T < T_N$. We have also labelled the region $T^{**} > T > T_S$ as intermediate magnetic crossover (intermediate).
- in Supplementary Materials Section 11 by adding the detailed explanation of a cross-over assignment to the temperature scale $T^{**} = 155$ K.

Second, the crux of the “extraordinary” phase transition is their observation of a Neel temperature. Besides questions about the error bars on this value (see below), there are already conflicting reports of TN in the literature, even from the same probes (e.g., neutron diffraction). Readers will therefore harbor some skepticism that (a) the observation that TN=140K is totally new, and (b) it should be taken at face value. Especially in van der Waals materials, the Neel temperature can be affected by all sorts of factors besides the probe itself (including how the sample was handled between measurements, c.f. RuCl3 http://dx.doi.org/10.1103/PhysRevB.93.134423).

We thank Reviewer #1 for bringing up the intriguing inconsistency in the T_N reported in literature for bulk CrSBr. We also noticed this phenomenon, and moreover, we think perhaps this variation of T_N in the literature is in fact consistent with our work of finding a surface AFM order onset and a bulk AFM onset. Please see our reasons below:

1) In the literature, the magnetic transition temperature for bulk CrSBr has been reported to be (a) 132K for **single crystal** CrSBr measured by neutron single crystal diffraction, μSR, heat capacity, magnetic susceptibility (see references: *Adv Mater 2020, 32, 2003240*, *ACS Nano 2022, 16, 15917−15926, Adv. Sci. 2022, 9, 2202467* and *Nat. Comm. 2022, 13, 4745*); and (b) 140K for **powder** CrSBr measured by neutron powder diffraction (see reference: *Nat. Comm. 2022, 13, 4745*). Please note that we skip the T_N reported for few-layer CrSBr as we focus on bulk CrSBr in our current study. Interestingly, they coincide with the bulk and surface AFM transition temperatures that we find in our study, respectively. For the single crystal case, the surface takes a much smaller portion than the bulk and therefore the surface signal is barely seen – as a result, most experiment techniques capture the bulk magnetic onset temperature. However, for the powder case, the surface to bulk ratio significantly increases, and it is possible that the surface contribution is big enough that the measurement becomes sensitive to the surface magnetic order. Therefore, our finding of having a higher surface AFM onset at 140K and a lower bulk AFM onset at 132K potentially reconciles the conflict in the reported T_N in the literature for bulk CrSBr.

2) Taking Reviewer #1's suggestion, we further performed the same RA SHG measurements and analysis on a sample prepared separately (referred as Sample 2). We also performed the fit of the temperature dependence of the electric dipole (ED) susceptibility tensor elements, using the functional form of $C_1^{ED} = A\,(T_s - T)^{\beta} + B$ for $T < T_s$ and $C_1^{ED} = B$ for $T \geq T_s$. Due to the kink at T_N = 132K known as the impact on the surface order from the bulk order, we limit our fit to data between the temperature range of 132K – 200K. For our two independent RA SHG measurements on two samples, the fitted surface onset temperatures are T_s = 140K ± 0.2K (Sample 1, sample for the main text Figure 5) and 140K ± 0.1K (Sample 2), respectively (see Figures R3a and R3c). The error represents the 95% confidence interval calculated from the standard deviations given by the fitting process. In addition, we note that the temperature dependent ED signals show a **notable kink** (i.e., change of curvature) near T_N = 132K for both measurements, which is consistent with the expectation/prediction that the bulk order at T_N = 132K impacts the surface order.

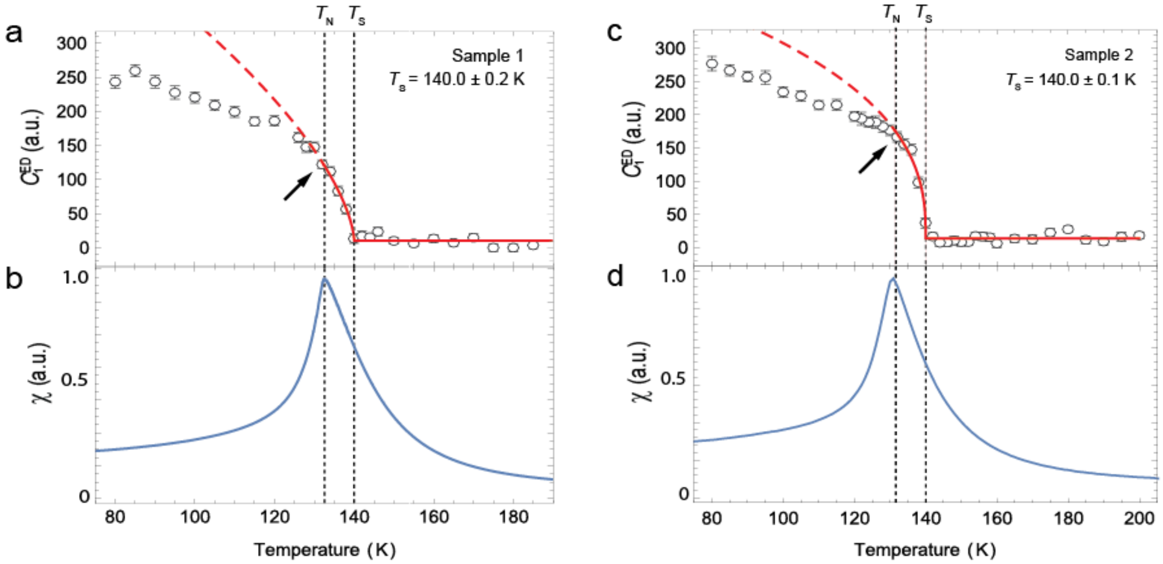

Figure R3 | Observation of enhanced surface magnetic transition temperatures in multiple samples. Surface ED SHG coefficient C_1^{ED} and magnetic susceptibility as a function of temperature measured from sample 1 (**a** and **b**) and sample 2 (**c** and **d**). The extracted transition temperatures are also labelled. Red curves show the best order-parameter fit using data for $T > 132$ K. Black arrows indicate the kinks at $T_N = 132$ K.

Furthermore, we performed temperature dependent magnetization measurements on Sample 1 and another sample from the same batch of Sample 2. For both samples, we can clearly see the bulk transition temperature at T_N = 132K ± 1K (see Figure R3b and R3d). Our bulk magnetism onset temperature is consistent with the literature values for bulk single crystal CrSBr.

With these results, we are confident about our finding of **two** separate phase transitions happening in 3D bulk CrSBr, namely, a surface phase transition at T_S = 140K ± 0.2K (or 140K ± 0.1K) and a bulk ordering onset at T_N = 132K ± 1K.

3) We fully agree with Reviewer #1 that the stacking sequence and atomic lattice variations can impact the magnetic properties for vdW magnetic systems (e.g., $RuCl_3$ pointed out by the reviewer). We worked to check the robustness of both the stacking sequence and the atomic lattice for CrSBr, using transmission electron microscopy (TEM). Although the sample preparation process of the TEM samples is more involved than the preparation of the RA SHG and magnetization measurements, the in-plane atomic resolution TEM images rarely show atomic defects (Figure R4a) and the cross-sectional TEM images consistently show the right overlying stacking between layers (Figure R4b). Therefore, we believe that the crystal structure of CrSBr is robust and that our sample is of high quality.

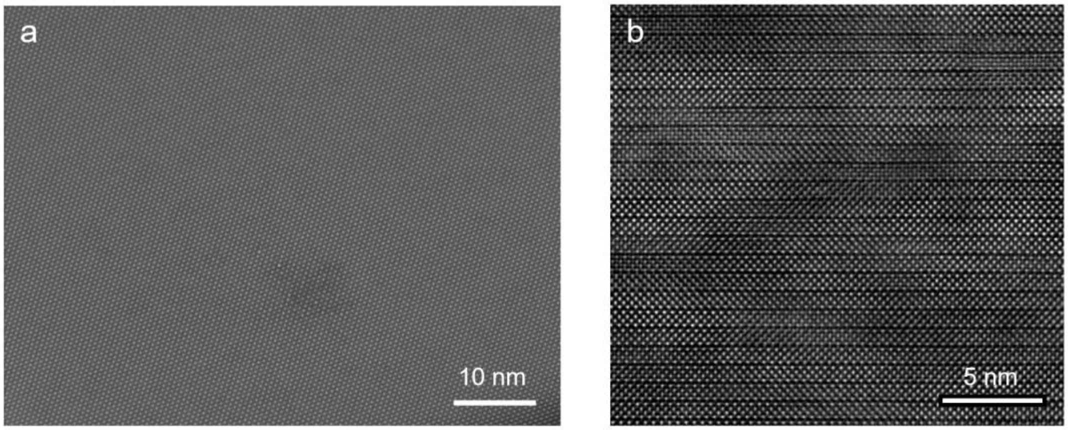

Figure R4 | Extensive TEM characterizations. a. wide-range atomic resolution TEM image of CrSBr in the *ab*-plane. **b** Side-view atomic resolution TEM image in the *ac*-plane.

In summary, we are confident about the presence of both a surface magnetic phase transition and a bulk magnetic phase transition in 3D CrSBr. Taking the terminology from the theoretical literature [*Phys. Rev. B 1975, 12: 3885-3901*], we refer the surface AFM transition at a higher onset temperature as a “surface” phase transition and the bulk phase transition at a lower onset temperature as an “extraordinary” phase transition. This finding potentially addresses the difference in the onset temperatures between single crystal and powder CrSBr reported in the literature.

Actions Taken:

1) We added discussions on the difference in the onset temperatures between single crystal and powder CrSBr and commented on our results in this context at the end of the first paragraph in Lines 200 – 207 of the main text:

> “Second, our surface AFM order onset temperature, T_S = 140 ± 0.2 K, coincides with the magnetic critical temperature reported for powder CrSBr measured with powder neutron diffraction[26] and bilayer CrSBr with SHG[21]. For powder CrSBr, it is true that the surface to bulk ratio significantly increases from that for single crystal CrSBr, and thus it is likely that the surface magnetism is detected by the powder neutron diffraction. For bilayer CrSBr, it resembles the surface magnetism in 3D CrSBr in the way that they both miss neighboring layers on one side. Therefore, our detection of T_S = 140 ± 0.2 K for the surface magnetic order in 3D CrSBr offers potential explanations for the variation in the magnetic critical temperature of CrSBr.”

2) We made sure to include the fitting error bars (95% confidence interval) for T_S in the main text.

3) We further added data of the additional RA SHG measurement on Sample 2 and magnetization measurements in Supplementary Materials Section 9, and added additional data of the in-plane and cross-sectional TEM images in Supplementary Materials Section 1.

Minor comments:

1. p. 2: “The transition establishing the bulk order, while the surface one is already present,” ← this is confusing wording. Consider rewording to “…while the surface is already ordered,”

We agree and thank Reviewer #1 for this suggestion. We have reworded the sentence.

Action taken: we updated the text in Lines 20 – 21 to be “… in the presence of the surface order…”

2. p. 3: “…CrSBr batch exhibits a clear order-parameter-like upturn at 140 K (Fig. 2e), a new temperature scale for 3D CrSBr crystals, not detected by any probes for bulk properties…” <-- It is perhaps a stretch to claim this is a new temperature scale. Given the previously reported TN=140K result for the bilayer (ref. 21), it seems that the authors here are simply stating that the energy scale of the surface is equal to that of a bilayer. Furthermore, anomalies at this temperature were observed in bulk magnetoresistance (ref. 24), so this temperature scale has been reported and discussed before for CrSBr.

We thank Reviewer #1 for pointing this out. We agree that our original statement was not accurate. We intended to motivate the surface origin of this order onset at 140K by illustrating its absence in many (but not all) bulk probe measurements. We have revised the statement accordingly.

Action taken: we have revised the text in Lines 93 – 95 to be “…CrSBr batch exhibits a clear order-parameter-like upturn at 140 K (Fig. 2e), a temperature that is hidden to many bulk-sensitive measurements for 3D CrSBr single crystals, for example, …”

3. Maybe I missed it, but do the authors report the thickness of the sample they measured?

The thickness of the two samples (Sample 1 and Sample 2) for RA SHG is about 0.2 mm. The thickness of the samples for the heat capacity and magnetization measurements is between 0.2 mm and 0.5 mm. The thickness of the samples for the TEM measurements is about ten layers thick for the in-plane measurement and a few nm for the cross-sectional measurement.

Action taken: We have added this information into the Method section.

4. Was the order parameter curve collected on heating or cooling, and what was the heating rate? When there are conflicting reports of TN, differences in heating/cooling rate are often the culprit, so this is important to report.

Our RA SHG data has been collected on warming up cycles, because we need to assure the single magnetic domain within the beam spot (~15 μm FWHM) for the data analysis. The heating-rate is about 0.5 K/minutes that is achieved through balancing the heater and the liquid nitrogen flow with a feedback loop in the Lakeshore temperature controller. Even after reaching the setpoint, we wait for another additional time (e.g., 5 minutes) to ensure the stability of the temperature. The RA SHG data has been taken at a temperature with a temperature stability of 0.005K.

Action taken: we added in the figure caption of Figure 5b and 5c that the data was taken during the warming-up cycle. And we add the heating rate information in the Method section.

5. The distinguishing of different domains via SHG is very clever work.

We thank Reviewer #1 for this compliment.

6. “Note that D is expected to be about the same in a single monolayer and in the bulk.” <-- Why? Naively, one would expect the additional broken symmetries on the surface to allow for more asymmetric exchange there than in the bulk (c.f. Moriya’s rules).

We agree with Reviewer #1 that the surface has a lower symmetry (point group *mm2*) than the bulk (point group *mmm*) and therefore may have different magnetic interaction parameters. Here, the easy-axis anisotropy D refers to the **intralayer** easy-axis anisotropy, which contains the single ion anisotropy and the exchange anisotropy. For the single ion anisotropy, it is a local property within the ligand-transition metal cage and therefore is not sensitive to the presence of neighboring layers. For the exchange anisotropy, the contribution from a neighboring layer is through the hopping path from Layer 1 to Layer 2 and then back to Layer 1, which should be much weaker than the contribution from the hopping pathways within Layer 1. Therefore, we think the intralayer easy-axis anisotropy D is comparable between with and without neighboring layers.

We further note that we did not consider the interlayer easy-axis anisotropy (D_{inter}) in the discussion, because it is a much smaller term comparing to the interlayer exchange coupling ($J_{\perp}$), intralayer easy-axis anisotropy (D), and intralayer exchange coupling $J_{||}$ (i.e., $D_{\text{inter}} << J_{\perp}, D << J_{||}$) and does not impact the physics noticeably.

Action taken: we have provided the reason for D being comparable in the monolayer and the bulk, by adding in Lines 231 – 233 “Here, D is dominated by the intralayer contributions and therefore is expected to be about the same in a single monolayer and in the bulk”.

7. The TN reported in the paper and fit in Fig. 2 panel (d) needs error bars to be compelling. The first data point below 140K is not outside error bars of the data points immediately to the right. Therefore it is statistically unjustified to treat it as the first point in the order parameter curve. This is especially important because the reports of finite intralayer ferromagnetism above TN would mean that one would see an upturn in the order parameter above TN, making it tricky to precisely nail down where the upturn begins. The authors should provide a fitted TN and \Beta exponent to compare with other studies, most notably Refs. 21, 23, and 26.

We thank Reviewer #1 for this comment. We have done the following analysis to provide the error bars for the onset temperature and to discuss the critical exponent β.

1) Please let us explain our SHG data first. Our SHG includes the bulk electric quadrupole (EQ) SHG contribution from the crystal structure ($\chi^{\text{EQ,structure}}$), the surface electric dipole (ED) SHG contribution from the surface magnetism ($\chi^{\text{ED,sAFM}}$), and the bulk EQ SHG contribution from the bulk magnetism ($\chi^{\text{EQ,bAFM}}$). Due to their different origin, $\chi^{\text{ED,sAFM}}$ scales **linearly** with the surface AFM order parameter ($\chi^{\text{ED,sAFM}} \propto \text{OP}_{\text{sAFM}}$), and $\chi^{\text{EQ,bAFM}}$ depends on the **quadratic** term of the bulk AFM order parameter ($\chi^{\text{EQ,bAFM}} \propto {\text{OP}_{\text{bAFM}}}^2$). Furthermore, because the bulk crystal structure point group is mmm and the bulk AFM order magnetic point group is $mmm1'$,

$\chi^{\mathrm{EQ,structure}}$ and $\chi^{\mathrm{EQ,bAFM}}$ have the same tensor form, and therefore, we cannot separate them in the experimental data and note them together as $\chi^{\mathrm{EQ}} \propto \mathrm{C} + \mathrm{OP_{bAFM}}^2$.

2) For the data in Figure 2e, it is the temperature dependent SHG intensity taken in the S_{in}-S_{out} channel at 40° between the light scattering plane and the crystal axis *a*. It results from an interference between the surface ED and bulk EQ contributions, which scales with the order parameter differently and cannot have a simple functional form fit. But given the data shows a clear onset around 140K, we can use an approximate functional form, $A\,(T_s - T)^{\beta} + B$, to extract T_{S} = 140K ± 1K. But the exponent β is not meaningful here.

3) To overcome the limitation of temperature dependent SHG intensity at a single angle, we need to perform temperature dependent RA SHG patterns and extract the temperature dependence of $\chi^{\mathrm{ED,}s\mathrm{AFM}}$ and χ^{EQ}, which contains the critical behaviors for order parameters. This is what we have done for Sample 1 in the main text Figure 5, and Sample 2 in Figure R3c. We have fitted T_{S} = 140K ± 0.2K for Sample 1 and T_{S} = 140K ± 0.1K for Sample 2, which is robust against the choice of temperature ranges. Unfortunately, the critical exponent, β, varies dramatically between different temperature ranges for fitting, being β = 0.6 ± 0.2 for Sample 1 and 0.4 ± 0.1 for Sample 2. Such a variation in β is due to the lack of data points between 132K and 140K and also the impact of the bulk onset at 132K.

Action taken: we have added in the error bars for T_{S} in both the main text and Figure S10 in the Supplementary Materials Section 9. We further commented on the inaccuracy of β in the Supplementary Materials Section 9.

8. Fig. 2 caption: "unreported onset at 140 K". Again, saying this temperature is "unreported" is a step too far. It was reported in few-layer compounds and in powder neutron diffraction and in magnetoresistance.

We thank the reviewer for pointing this out, and we have changed the description in the Figure 2 caption.

Action taken: we change the caption of Figure 2 to be "…Temperature dependent SHG intensity in the S_{in}-S_{out} channel at the angle $\phi = 40°$ revealing an onset at ~140 K for bulk CrSBr, different from the bulk T_N = 132 K…"

Summary:
The main result is that the Neel temperature from SHG is greater than the Neel temperature from the bulk. However, there is already conflicting accounts of the Neel temperature in neutron diffraction (Ref. 23 vs. 26), so if I play the skeptic, I would say that this could be a discrepancy in sample quality, experimental protocol, or some other artifact. Furthermore, the authors should explain more the why they believe they are not simply observing the "intralayer correlations" discussed by others.

That said, the authors have done a very good job in their data collection and treatment, and the DFT results are quite compelling. Given appropriate revisions, this paper would be suitable for publication in Nature Communications.

We thank Reviewer #1 for the careful review of our manuscript and the constructive suggestions to improve the manuscript. We further appreciate the positive comments on our work.

We hope that through this revision, our additional data, in-depth discussion/explanation, and cross comparison with literature convince Reviewer #1 the presence of three temperature scales in 3D CrSBr through our RA SHG measurements: T^{**} = 155K that appears as a signal increase in the EQ SHG contribution; T_S = 140K that shows up as an order-parameter-like onset in the ED SHG signal; and T_N = 132 K that manifests as a clear kink in the ED SHG contribution. We also confirmed by heat capacity and magnetization measurements that T_N = 132 K for our CrSBr single crystals. With these, I hope we addressed Reviewer #1's concerns satisfactorily.

We thank Reviewer #1 again for his/her positive and helpful evaluation of our manuscript.

Reviewer #2 (Remarks to the Author):

I reviewed the paper by Guo et al entitled "“Extraordinary” Phase Transition Revealed in a van der Waals Antiferromagnet", which include SHG experiments, HAADF-STEM, and ab initio simulations on the different critical temperatures observed in CrSBr at the surface and at the inner bulk part of this compound. The paper discusses the possibility to stabilize different phase transitions at the bulk and surface as measuring the surface-sensitivity dipole moments. I'd have a few comments on this manuscript that would restrict its acceptance. I would recommend a full revisions of this manuscript, and send it to a more technical journal.

We thank Reviewer #2 for his/her time and effort in reviewing our manuscript. Please allow us to explain the significance of our work that supports its suitability for Nature Communications.

1. The main experimental finding of this work is the split of 8K between the surface and the bulk magnetic phase transitions. Counterintuitively and importantly, the surface magnetism onset temperature is higher than the bulk one. This phenomenon was predicted in the 1970s [*Phys. Rev. B 1974, 9: 2194-2214* and *Phys. Rev. B 1975, 12: 3885-3901*], remains being actively studied until now [*Phys. Rev. Lett. 2021, 127, 120603*], but has been rarely observed in real materials. Because such a phenomenon is counterintuitive and was thought to be rare, the theorists who predicted the split surface-bulk transitions gave the names “extraordinary” (i.e., bulk) and “surface” phase transitions for these two separated phase transitions. Our work shows that vdW layered compounds are ideal platforms for exploring such physics of separated surface and bulk phase transitions. While we demonstrated it in vdW magnets, this physics is not limited to magnetism, but can be generalized to other spontaneous symmetry-breaking phase transitions when the required conditions on the interaction parameters are met. Therefore, we believe our work opens the experimental pathways towards enriching the phase diagrams of symmetry-breaking phase transitions via distinct surface and bulk interactions, which will be of interest to scientists in condensed matter physics, materials science, surface science, and nanoscience.

2. The key experimental technique that allowed for this important, yet previously missed finding is our rotational anisotropy second harmonic generation (RA SHG) that operates in the oblique incidence geometry and across a wide temperature range. Our RA SHG is unique and powerful in a sense that it detects both **(1)** inversion symmetry breaking surface signal through the electric dipole (ED) SHG contribution and **(2)** inversion symmetry preserved bulk signal through the electric quadrupole (EQ) SHG contribution, and that **(3)** it uses the interference of ED and EQ SHG signals to detect the full broken symmetries, capture the critical behaviors across phase transitions, and resolve the magnetic domains. This level of insightful knowledge obtained by our RA SHG is hardly achievable by conventional SHG techniques that primarily focus on the ED SHG from noncentrosymmetric sources. Therefore, we believe our experimental technique is novel and important for future research in studying phase transitions, especially the complex phase transitions. This will be of interest to both the optics community and the materials science and condensed matter physics communities.

Our work demonstrates an important scientific discovery made by a novel experimental technique, which is of broad interest to optics, condensed matter physics, materials science, surface science, and nanoscience communities. Thus, we believe this work is suitable for Nature Communications.

Please see our detailed responses to the questions below.

1) It is well known in the field that different samples (from different groups) can give different transition temperatures since we haven't achieved any standard guidelines or receipts that would allow the control of defects, step-edges, grain-boundaries, surface roughness, etc. 2D magnetic materials are still far way from more standard protocols in place for other materials, e.g. graphene, TMDs, h-BN, etc. So, further measurements on different samples, produced in different way would be helpful to sort the variations in temperature observed.

We agree with Reviewer #2 that the crystal quality is key to the magnetic phase transitions in vdW magnets. We have taken very careful examinations of the sample quality of our CrSBr single crystals. We have also reproduced our experimental results in different samples. Below we will demonstrate the robustness of our result in three steps.

1. Consistent T_N and T^{**} with the literature report

We would like to clarify that we observe the onset temperature of T_S = 140K, in addition to our successful detection of the known bulk magnetic onset temperature of T_N = 132K and the previously reported intermediate magnetism temperature scale of T^{**} = 155K. In another word, we not only **reproduced the reported temperature scales** in our CrSBr single crystals, confirming our sample quality, but also **revealed an additional onset temperature** of 140K in the very same samples. Please see the specific experimental evidence below.

- In the RA SHG data of 3D CrSBr (Figures 5b and 5c of the main text and Figures R5a and 5b), we can clearly identify three temperature scales: T^{**} = 155K that appears as a signal increase in the EQ SHG contribution; T_S = 140K that shows up as an order-parameter-like onset in the ED SHG signal; and T_N = 132 K that manifests as a clear kink in the ED SHG contribution.
- In magnetic susceptibility measurements of 3D CrSBr, we clearly detect T_N = 132 K as a clear peak on the very same sample where RA SHG measurements in Figure R5a and 5b were taken (Figure 5d of the main text and Figure R5c).
- In heat capacity measurements of 3D CrSBr, we can also capture T^{**} = 155K that appears as a broad hump and T_N = 132 K that shows up as a small but sharp peak (Figure 2d of the main text and Figure R5d).

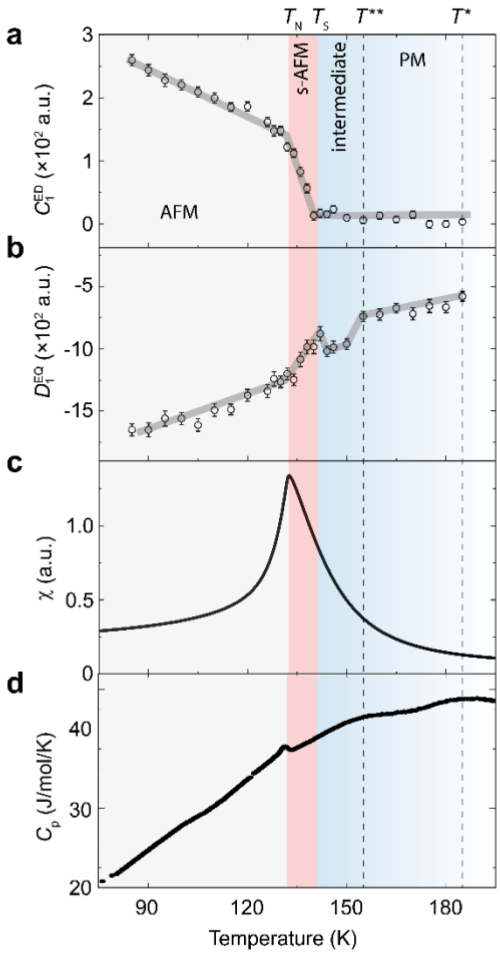

Figure R5 | Observation of different temperature scales. **a**, ED SHG coefficient C_1^{ED} and **b**, EQ SHG coefficient D_1^{EQ} as a function of temperature. Grey curves serve as guides to the eyes. **c**, Magnetic susceptibility as a function of temperature measured under 1000 Oe magnetic field along the *b*-axis. **d**, heat capacity as a function of temperature. The regions of paramagnetism (PM), intermediate magnetic crossover (intermediate), surface antiferromagnetism (s-AFM) and bulk antiferromagnetism (AFM) are shaded in different colors, with their characteristic temperatures marked.

2. High crystalline quality of our CrSBr single crystals

For vdW layered materials, the major factors that influence the crystal quality are the in-plane atomic lattice and the out-of-plane stacking sequence. Furthermore, for optical measurements, we also care about the surface flatness and crystalline steps. We have performed structure characterizations to establish the high crystalline quality and surface quality of our CrSBr single crystals.

1) Atomic resolution transmission electron microscopy (TEM) survey
   - To check the in-plane atomic lattice, we have performed the scanning TEM (STEM) measurements over thin layer CrSBr, where individual atomic defects can be visualized. A representative atomic resolution STEM image of about 10 layers CrSBr is shown in Figure R6a over an *ab*-plane area of 70 x 50 nm^2. The orthorhombic atomic lattice can be clearly seen. Furthermore, within this field of view, no single atomic defects were detected. Assuming each atomic defect takes approximately 0.5 x 0.5 nm^2 based on the STEM measurement of the lattice parameters, this provides an upper bound of atomic defect concentration of 0.5 x 0.5 nm^2 / 70 x 50 nm^2 x 100% ≈ 0.01%. We note that surveys over different samples and locations **consistently show a very low atomic defect concentration**.
   - To examine the out-of-plane stacking sequence, we have performed the cross-sectional STEM measurement, where the interlayer stacking can be clearly shown. A representative cross-sectional STEM image is displayed in Figure R6b over an *ac*-plane area of 22 x 20 nm^2. A perfect overlaying stacking geometry with no stacking faults is observed. We have examined multiple locations over this specimen and **found no stacking faults**. This finding intuitively makes sense as there are no degenerate stacking states (i.e., only one stacking possibility) for this overlaying stacking geometry, in contrast to the graphene case where there are more than one degenerate rhombohedral stacking states (e.g., ABC v.s. ABA) that can lead to stacking faults.

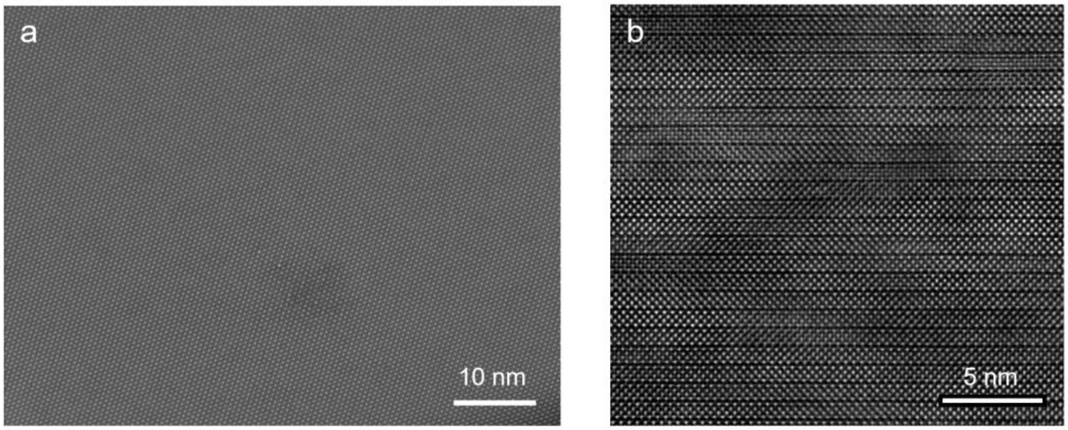

Figure R6 | Extensive TEM characterizations. a. Wide-range atomic resolution TEM image of CrSBr in the *ab*-plane. **b.** Wide-range side-view atomic resolution TEM image in the *ac*-plane.

2) Atomic force microscopy (AFM) survey

- AFM captures the surface roughness and atomic steps, with a height resolution of ~ 0.1nm. Figure R7a shows a representative AFM image taken over a CrSBr sample where we performed RA SHG measurement. Over an area of about 130 x 140 μm^2, we only observed a few atomic step sizes of height ~1-2nm in the lower right corner of a 30 x 55 μm^2 area (see a linecut in Figure R7b). For the rest of the field of view, it is a single atomic terrace with a standard deviation of height of 0.086 nm and a FWHM of the height of 0.2 nm (see the histogram of height distribution in Figure R7c). Therefore, our CrSBr single crystals with freshly cleaved surfaces show **highly flat surfaces with low density of atomic defects**.

  We further note that CrSBr crystals show high stability in the ambient environment, which assures that our sample preparation process does not introduce imperfections.

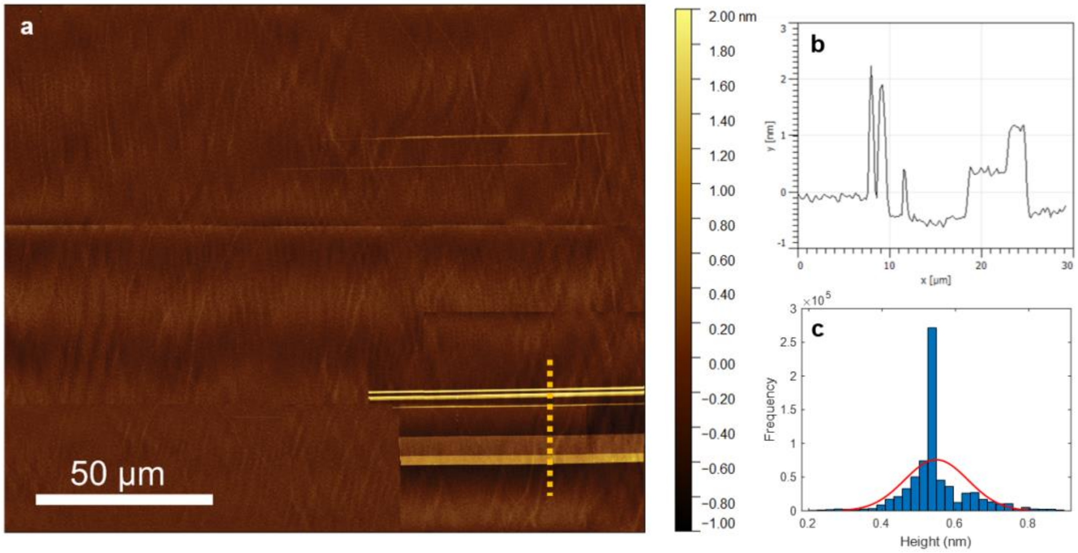

Figure R7 | AFM characterization of CrSBr sample. a. AFM image taken over a CrSBr sample. **b**. Linecut height profile indicated by the yellow dash line in **a**. **c**. Histogram of height distribution from the flat region. The red curve indicates the Gaussian fit, yielding the standard deviation to be 0.086 nm.

3. Reproducibility of the same results in different samples

To confirm the reproducibility of our results, we chose CrSBr single crystals from two different growth batches and performed both the RA SHG and magnetization measurements on them. A representative result is shown in Figure R8. The ED SHG contribution shows T_S = 140K onset for the surface AFM state and captures T_N = 132K kink caused by the bulk AFM order (Figures R8a and R8c) on both Sample 1 and Sample 2. The magnetization data clearly detects T_N = 132K for the onset of the bulk AFM order (Figures R8b and R8d) for both samples.

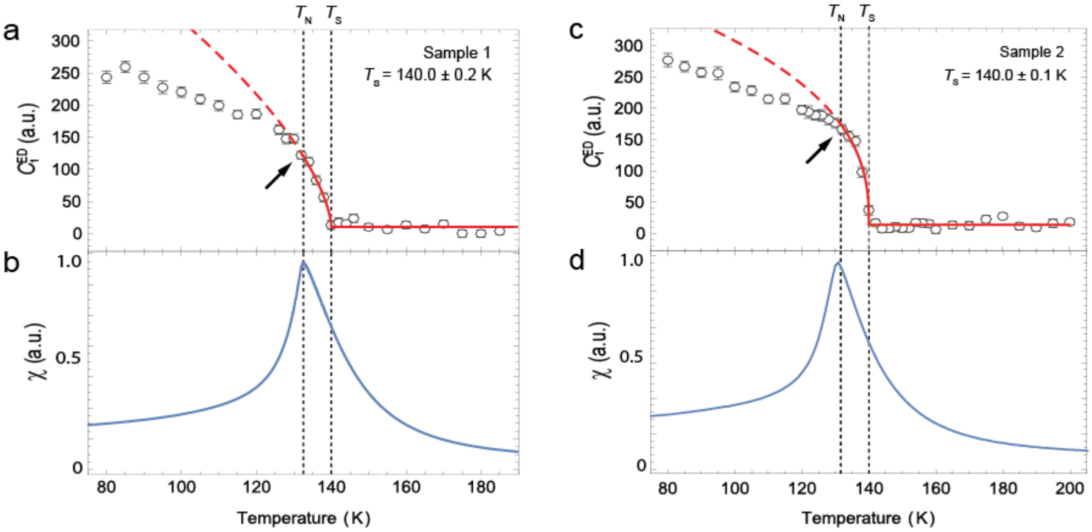

Figure R8 | Observation of enhanced surface magnetic transition temperatures in multiple samples. Surface ED SHG coefficient C_1^{ED} and magnetic susceptibility as a function of temperature measured from sample 1 (**a** and **b**) and sample 2 (**c** and **d**). The extracted transition temperatures are also labelled. Red curves show the best order-parameter fit using data between T_N = 132 K and T_S = 140 K. Black arrows indicate the kinks at T_N = 132 K.

In summary, the presence of T_S = 140K on top of T_N = 132K and T^{**} = 155K in our 3D CrSBr has been convincingly shown in different samples out of different growth cycles. At the same time, our samples do consistently reproduce T_N = 132K (and T^{**} = 155K) that is reported in the literature. Furthermore, our CrSBr single crystals show very low atomic defect concentrations, almost absence of stacking faults, highly flat surfaces, and low density of atomic steps at the surfaces after proper mechanical exfoliations, all of which consistently support high crystalline quality of our CrSBr samples.

Action taken: We have added a sentence in Lines 184 – 186 to clarify the coexisting multiple temperature scales in our CrSBr single crystals, "Three important temperature scales are captured in the temperature dependence of ED and EQ contributions, T^{**} = 155 K, T_S = 140 K, and T_N = 132 K that are discussed in-depth below."

We added in Supplementary Materials Section 1 and Section 2 the confirmation of high crystalline quality and surface quality by STEM and AFM measurements.

We further added in Supplementary Materials Section 9 the reproduced results in different CrSBr samples from different growth batches.

2) It is really not convincing the way it is separated contributions from inner bulk and surface. I understand the difficulties to try to deconvolutionate the signal, which even so, it would not be clear. I looked for some information of any penetration depths in the measurements, or some plot showing the SHG vs. penetration depth, but nothing is included. Without knowing this information, not much can say about different temperatures at the surface and inner bulk. Moreover, penetration depths would only provide part of the solution since it could also be the case that the layers are only probed until certain thickness, and the rest not. So, it doesn't mean that the surface

might have a different transition temperature, relative to bulk, but only a few layers would be considered. There is no simple solution for this problem though.

We appreciate this thoughtful question by Reviewer #2, which is actually one key point of our manuscript. As Reviewer #2 pointed out, the separation of surface and bulk cannot be done through identifying a depth d_c above/below which is considered as surface/bulk.

The way that we use to separate the surface contribution and the bulk contribution is based on distinct symmetries between them. Reviewer #2 accurately proposed this concept in his/her Question 3 right below, but questioned our capability of distinguishing different symmetry point groups for surface and bulk. In the answer to Question 3, we will show that our RA SHG is capable of distinguishing the symmetries and that is why we believe our technique is novel and powerful.

3) Following up from my previous comments, normally the best way to try to solve this uncertainty between bulk and surface is to have materials with different crystal symmetries; or the same one, but in different crystal phase. I can see that the authors characterised the crystals (Figure 2), which seems in good crystallinity across the thickness. So, there is not simple way to separate contributions from the surface from those in the bulk.

As Reviewer #2 pointed out that the most efficient way of distinguishing surface and bulk is via symmetries, we indeed leveraged this distinction in symmetries to separate the SHG signals from surface and bulk, because they do show distinct RA SHG fields.

Below please first allow us to go through our analysis procedure.

1. Symmetry properties of the surface and the bulk.

Reviewer #2 is correct that the in-plane atomic arrangement and the out-of-plane stacking sequence do not change between bulk and surface for 3D CrSBr. Nevertheless, they show different symmetries. To any point in the inner bulk, both sides are CrSBr samples, and it has the bulk crystalline point group *mmm*. However, to the surface, one side is vacuum (or ambient) whereas the other side is CrSBr. As a result, the surface lacks the following symmetries that connects the vacuum (or ambient) side to the CrSBr side: spatial inversion, mirror parallel to the *ab*-plane, 2-fold rotational axis along the *a* and *b* axes, and it ends up with the surface crystalline point group *mm2*. Similarly, in the layered AFM phase, although the spins share the same arrangement across the entire sample, the surface still has a different magnetic point group (*m'm2'*) from the bulk magnetic point group (*mmm1'*).

We summarize the point groups for surface and bulk across different temperature ranges in Table 1 below.

Table 1. Symmetries at the surface and inside the bulk

	T > 140 K paramagnetic	140 K ≥ T > 132 K surface AFM	T ≤ 132 K surface + bulk AFM
Bulk	*mmm* (EQ)	*mmm* (EQ)	*mmm1'* (EQ)
Surface	*mm2* (ED)	*m'm2'* (ED)	*m'm2'* (ED)

2. Differentiation and determination of the ED and EQ SHG sources.

From Table 1, we can see that the surface structural and magnetic point groups are subgroups of their bulk counterparts. For the case of 3D CrSBr, the surface point groups, *mm2* and *m'm2'*

break the spatial inversion symmetry, whereas the bulk point groups, *mmm* and *mmm1'*, **preserve** the spatial inversion symmetry. As a result, the surface supports the electric dipole (ED) SHG that is allowed by the broken spatial inversion symmetry, and the bulk needs to call for the electric quadrupole (EQ) SHG because its ED SHG is forbidden by the presence of spatial inversion symmetry in the bulk.

Because of the different radiation processes, surface ED v.s. bulk EQ, of SHG under different symmetry point groups, they will show distinct RA patterns, which we rely on to separate the surface and bulk contributions at different temperature ranges.

- **For $T > T_S$:** using this concept, we can determine the necessity of bulk EQ SHG for explaining the RA SHG data at $T > T_S$. Shown in Figure R9 below, the first row shows RA SHG patterns taken in all four polarization channels at $T = 185$ K (i.e., $T > T_S$). The second row displays the simulated RA SHG patterns for the four polarization channels, using bulk EQ SHG contribution under the centrosymmetric structural point group *mmm*. The third row shows the simulated RA SHG patterns for the four polarization channels, using surface ED SHG contribution under the noncentrosymmetric structural point group *mm2*. Our data definitely needs the bulk EQ SHG to interpret and may or may not require the surface ED SHG (but only the surface ED SHG is not sufficient due to its zero signal in the S_{in}-S_{out} channel).

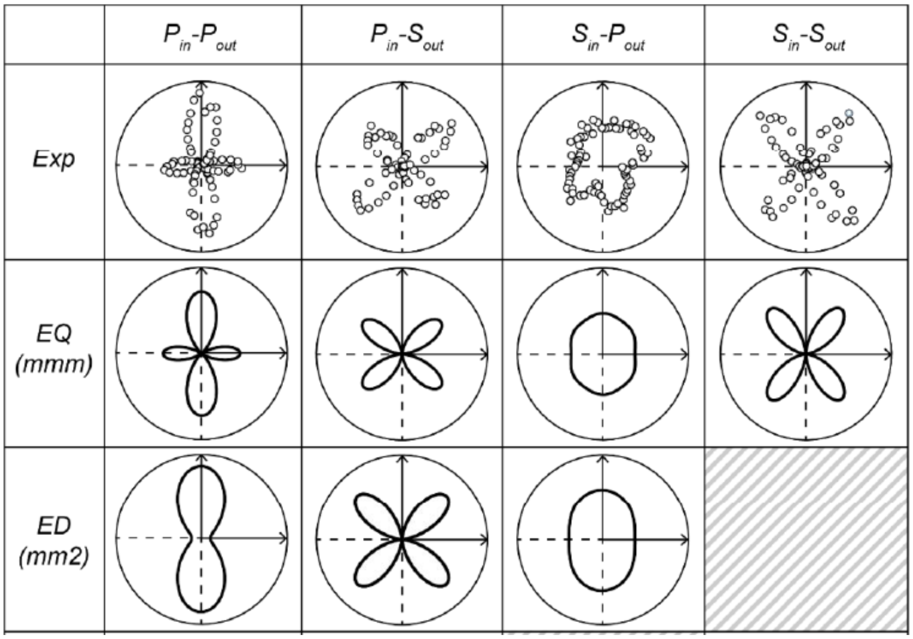

Figure R9 | Comparison between experiment data (*Exp*) and simulations for EQ SHG radiation from *mmm*, and surface ED SHG radiation from *mm2*. The ED SHG does not align with our experiment data.

- **For $T \leq T_S$:** following the same concept, we know that the highly **asymmetric** RA SHG patterns, taken in the magnetic phase ($T \leq T_S$), cannot be explained by the bulk EQ SHG alone or by the surface ED SHG solely, but requires an interreference between the surface ED and the bulk EQ SHG. Figure R10a shows the RA SHG pattern in the S_{in}-S_{out} channel at $T = 80$ K. Its asymmetric pattern is in stark contrast to the bulk EQ SHG from either the structural (*mmm*) or the magnetic (*mmm1'*) contributions, which are identical (Figure R10b), the surface ED SHG from the structural (*mm2*) contribution that is absent (Figure

R9 third row, fourth entry, or Figure R10c), and the surface ED SHG from the magnetic (*m’m2’*) contribution (Figure R10d). These exclusions of sole sources above naturally lead us to the consideration of interference between different sources. Here, we have **only one** interference option: the bulk EQ SHG under *mmm* or *mmm1’* point group and the surface ED SHG under *m’m2’* point group.

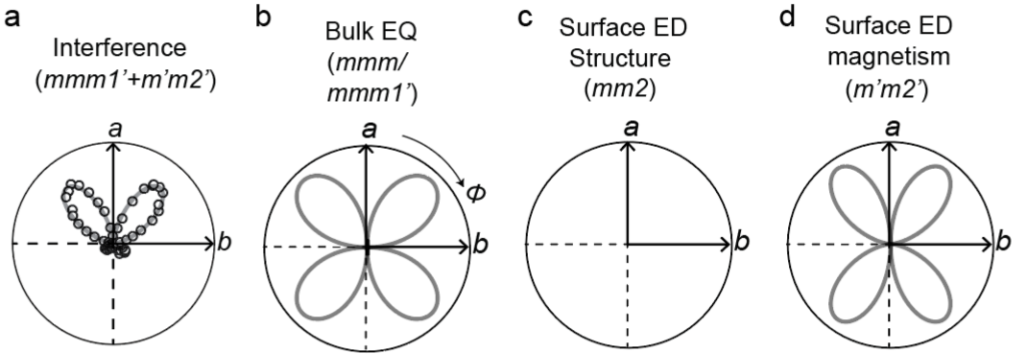

Figure R10 | Comparison between SHG RA patterns in the S_{in}-S_{out} channel between experiment data (white circles in **a**), EQ SHG from bulk (*mmm/mmm1’*) in **b**, ED SHG from surface structure (*mm2*) in **c**, ED SHG from surface magnetism (*m’m2’*) in **d**, and the interference between EQ SHG from bulk and ED SHG from surface magnetism (solid curve in **a**).

3. Fitting functional forms based on the identified SHG sources.

From the discussion in point 2 above, we know that the RA SHG patterns across the wide temperature range (80 – 140 K) can only come from the interference between two sources, the bulk EQ SHG under *mmm* (same as *mmm1’*) and the surface ED SHG under *m’m2’*. Using the RA SHG in the S_{in}-S_{out} channel as an example:

- For the surface ED SHG under *m’m2’*, the electric field functional form is expressed as

$$E^{\mathrm{SS,surface\ ED}}(\varphi) = (\chi_{\mathrm{xyy}} + 2\chi_{\mathrm{yxy}})\mathrm{Cos}[\phi]^2\mathrm{Sin}[\phi] + \chi_{\mathrm{xxx}}\mathrm{Sin}[\phi]^3$$

- For the bulk EQ SHG under *mmm* or *mmm1’*, the electric field functional form is shown as

$$E^{\mathrm{SS,bulk\ EQ}}(\varphi) = -\mathrm{Sin}[\theta]((\chi_{\mathrm{xyxy}} + 2\chi_{\mathrm{yyxx}} - \chi_{\mathrm{yyyy}})\mathrm{Cos}[\phi]^3\mathrm{Sin}[\phi] + (\chi_{\mathrm{xxxx}} - 2\chi_{\mathrm{xxyy}} \\ - \chi_{\mathrm{yxyx}})\mathrm{Cos}[\phi]\mathrm{Sin}[\phi]^3)$$

- For the total SHG intensity, it is the interference between $E^{\mathrm{SS,surface\ ED}}$ and $E^{\mathrm{SS,bulk\ EQ}}$, shown as

$$I^{\mathrm{SS}}(\varphi) = \left(E^{\mathrm{SS,surface\ ED}} + E^{\mathrm{SS,bulk\ EQ}}\right)^2 \\ = ((\chi_{\mathrm{xyy}} + 2\chi_{\mathrm{yxy}})\mathrm{Cos}[\phi]^2\mathrm{Sin}[\phi] + \chi_{\mathrm{xxx}}\mathrm{Sin}[\phi]^3 - \mathrm{Sin}[\theta]((\chi_{\mathrm{xyxy}} + 2\chi_{\mathrm{yyxx}} \\ - \chi_{\mathrm{yyyy}})\mathrm{Cos}[\phi]^3\mathrm{Sin}[\phi] + (\chi_{\mathrm{xxxx}} - 2\chi_{\mathrm{xxyy}} - \chi_{\mathrm{yxyx}})\mathrm{Cos}[\phi]\mathrm{Sin}[\phi]^3))^2$$

We use the functional form of $I^{\mathrm{SS}}(\varphi)$ to fit our RA SHG pattern in the S_{in}-S_{out} channel, where χ_{ijk}^{ED} and $\chi_{ijkl}^{\mathrm{EQ}}$ are the surface ED and bulk EQ SHG susceptibility tensor elements, respectively. We note that from the fit, we can get the four coefficients in front of the trigonometric polynomial terms, which are linear superpositions of either χ_{ijk}^{ED} or $\chi_{ijkl}^{\mathrm{EQ}}$, but not both (i.e., none of the coefficients is a mix of χ_{ijk}^{ED} and $\chi_{ijkl}^{\mathrm{EQ}}$). That is: $C_1^{\mathrm{ED}} = \chi_{xyy}^{\mathrm{ED}} + 2\chi_{yxy}^{\mathrm{ED}}$ and $C_2^{\mathrm{ED}} = \chi_{xxx}^{\mathrm{ED}}$ for the ED contribution, and $D_1^{\mathrm{EQ}} = \chi_{xyxy}^{\mathrm{EQ}} + 2\chi_{yyxx}^{\mathrm{EQ}} - \chi_{yyyy}^{\mathrm{EQ}}$ and $D_2^{\mathrm{EQ}} = \chi_{xxxx}^{\mathrm{EQ}} - 2\chi_{xxyy}^{\mathrm{EQ}} - \chi_{yxyx}^{\mathrm{EQ}}$ for the EQ contribution. So, our fitting can confidently separate out the ED and EQ contributions, although we cannot get individual tensor element values.

4. Understanding the physical meaning of the fitted results

We notice that these coefficients contain either only ED or only EQ tensor elements. We further know that all the elements in the ED tensor scale **linearly** with the surface AFM order parameter, and that all the elements in the EQ tensor depend on the **quadratic** of the bulk AFM order parameter. Therefore, we get that the coefficients C^{ED}, a linear combination of χ_{ijk}^{ED}, should scale linearly with the surface AFM order parameter, and the coefficients D^{EQ}, a linear combination of $\chi_{ijkl}^{\mathrm{EQ}}$, should contain the quadratic of the bulk AFM order parameter, which allows us to separate and determine the phase transitions of the corresponding orders.

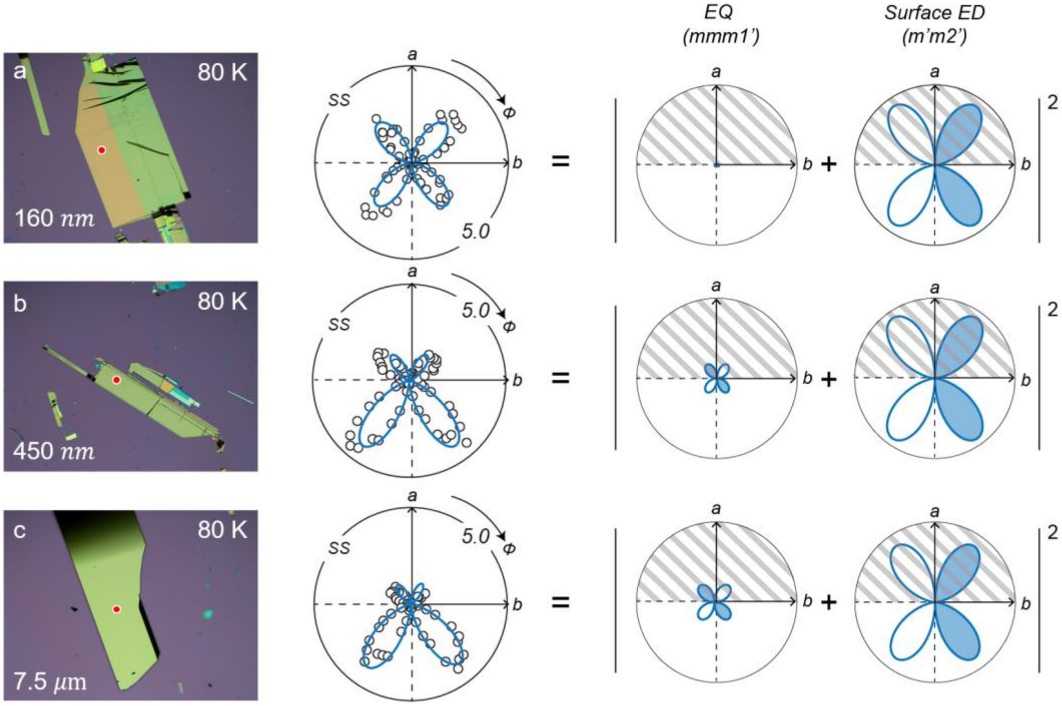

Figure R11 | Thickness dependent SHG RA. Optical image, bulk EQ and surface ED SHG contributions and their interference for samples with thickness **a**. 160 nm **b**. 450 nm and **c**. 7.5 μm. All the patterns are measured at 80 K. Red dots in the optical images indicate the location for SHG measurements.

In addition to this analysis procedure, we are also motivated by Reviewer #2' question to double check the surface and bulk origins of the two contributions to the SHG in 3D CrSBr. We performed **thickness dependent measurements** and carried out the same analysis. We investigated 3 different thickness, 160nm, 450nm, and 7500nm (7.5 μm) that are quantified by the atomic force microscopy measurements. In Figure R11, we show their RA SHG patterns in the S_{in}-S_{out} channel and their decompositions into the bulk EQ and surface ED contributions. We can clearly see that:

a) As the thickness increases, the surface ED SHG contribution stays nearly the same. This is consistent with its surface nature.
b) In contrast, when the thickness increases, the bulk EQ SHG contribution, increases which is also consistent with its bulk nature. From the trend, we can also roughly estimate our **light penetration depth is slightly deeper than 450nm**. This estimation is consistent with what we can extract from a recent publication [*Adv. Funct. Mater. 2023, 2307259*]: the penetration depth is approximately 700nm for 800nm incident light.

In summary, our analysis can separate the ED and EQ contributions based on their different radiation processes and different point symmetries. We further confirmed the surface nature of the ED SHG and the bulk nature of the EQ SHG through the additional thickness dependence study.

Action taken: We added the fitting procedure in the Method section. We further included the thickness dependent results in Supplementary Materials Section 7.

4) About the SHG signal at 80 K (Fig 3c,3d), domain A/B, which translate in Figure 4b, both situations are possible. However, it does not mean that a phase transition is taking place differently at the surface and inner bulk. My impression looking at this dataset is that the authors are measuring how two possible magnetic coupling may exist at the same temperature, which indicates the meta-magnetic character of CrSBr. Other 2D magnets don't show this, but it doesn't mean different phase transitions at different parts of the crystal though.

We thank Reviewer #2 for sharing his/her thoughts here. We agree with him/her that Figures 3c and 3d are not used to support the separation of surface and bulk magnetic phase transitions, because the separation of the two phase transitions can only be seen via our careful **temperature dependent** RA SHG measurements shown in Figure 5 of the main text and reproduced in a different sample in Figure R8 in the response to Reviewer #2's question 1 above.

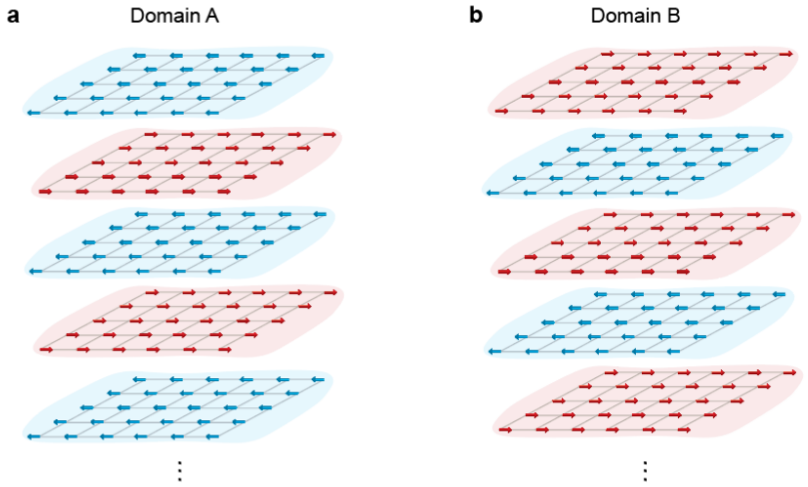

Figure R12 | Illustrations for the spin texture in CrSBr at $T < T_N$ in **a**. domain A and **b**. domain B

We show Figures 3c and 3d to prove that there are in total two degenerate magnetic ground states at low temperature ($T < T_N$): being left/right/left/right… and right/left/right/left… ("left" and "right" refer to spin along the positive and negative directions along the *b*-axis), as illustrated in Figure R12 above. These two states are related by a 2-fold rotational symmetry or a time-reversal symmetry or a vertical mirror parallel to the spin direction (i.e., *b*-axis). These two degenerate domain states are similar to the spin-up and spin-down domain states for a simple ferromagnet.

These two magnetic domain states have the same energy and should have **equal probability to show up** in a macroscopically large sample and/or through multiple thermal cycles. And indeed, we can find both states in our RA SHG measurements. And their presence does not mean different phase transitions for the bulk and the surface.

Action taken: We have added the connection between the magnetic domain states and the RA SHG data in Figures 3c and 3d by adding a sentence in Lines 123 – 125: "…, and therefore, confirms that they correspond to the two degenerate magnetic domain states, $\leftarrow\rightarrow\leftarrow\rightarrow\cdots$ (Domain A) and $\rightarrow\leftarrow\rightarrow\leftarrow\cdots$ (Domain B), where $\leftarrow/\rightarrow$ represents the spins within individual layers aligning along the negative/positive direction of the *b*-axis".

5) The theoretical part is very simple with several limitations on the description of the interactions, system, etc. In particular, the spin Hamiltonian included at the end of the manuscript (no number referring to it in the text!) corresponds to only exchange interactions, without any anisotropy terms, dipolar interactions, DMI, etc. Indeed, CrSBr has a biaxial magnetic anisotropy which needs to be taken into account to produce accurate results.

We agree with Reviewer #2 that we used a simplified spin Hamiltonian that includes the intralayer exchange coupling up to the 7th nearest neighboring exchange ($J_{1\text{-}7}$), but not interlayer exchange coupling or anisotropies. At the same time, we would like to explain that such a spin Hamiltonian is sufficient in grasping the trend of the mean-field magnetic transition temperature. The mean field Néel temperature (T_N) of bulk CrSBr is dominated by the Curie-Weiss temperature (T_CW) of monolayer CrSBr with a small correction from the interlayer exchange coupling and anisotropies, where T_CW is determined by the intralayer exchange couplings ($J_{1\text{-}7}$) via $T_\mathrm{CW} = -\frac{1}{3}(\mathrm{S}+1)\,(2J_1 + 4J_2 + 2J_3 + 4J_4 + 4J_5 + 2J_6 + 4J_7)$. The relationship between T_N and T_CW is mainly captured by the expression, $T_\mathrm{N} \approx \frac{T_\mathrm{CW}}{A+\log(J_{||}/J')}$, where A is a constant of about 3-5; $J_{||}$ is the average characteristic intralayer exchange coupling; and J' represents a properly-defined combination of the interlayer coupling $J_\perp$ and the easy-axis anisotropy D.

Because the anisotropy terms only enter the denominator logarithmically, its impact to T_N is very small. A rough estimation can be done to see the impact of anisotropy terms on T_N. If the change of anisotropies causes a 10% change of J', it will only lead to a change of the denominator by a value of $\log(90\%) = -0.046$ (i.e., $\log\left(\frac{J_{||}}{0.9J'}\right) = \log\left(\frac{J_{||}}{J'}\right) - \log(0.9)$), which is much smaller than the constant A ~ 3-5, as well as $\log\left(\frac{J_{||}}{J'}\right)$, and cause a very minor impact on T_N.

Therefore, the Néel temperature T_N is dominated by the Heisenberg intralayer exchange coupling via T_CW and may get minor corrections from the anisotropy terms.

Furthermore, recent experimental results on spin waves via inelastic neutron scattering [*Adv. Sci. 2022, 9, 2202467*] also support that the isotropic Heisenberg model is sufficient in interpreting the spin wave dispersion in bulk CrSBr. This finding further supports the *smallness* of the anisotropy in bulk CrSBr and justifies our choice of the simplified spin Hamiltonian in our study.

Action taken: We added the discussion of the impact from the anisotropy on the bulk Néel temperature and justify the choice of an isotropic Heisenberg spin model (refer to the spin Hamiltonian in the Method Section) in Lines 239 – 243: "… of an isotropic Heisenberg spin Hamiltonian (see Methods), … Our choice of isotropic Heisenberg spin Hamiltonian here is supported by the fact that the influence on T_{N} by the magnetic anisotropy is considered in $T_{\mathrm{N}} \approx \frac{T_{\mathrm{CW}}}{A+\log(J_{||}/J')}$ and is known to be logarithmically small."

6) Moreover, the equation for T_N referred to 'Mermin-Wagner formula', cited Ref.44, has nothing to do with the Mermin-Wagner's PRL paper in 1966, but rather by the S Todo's lab in 2005. Proper acknowledgment needs to be included. So, I'd suggest the authors to refer to Ref. 44, and remove the term 'Mermin-Wagner' throughout the paper, which nothing has to do with that.

We thank Reviewer #2 for pointing this out. Yes, we agree that the equation $T_{\mathrm{N}} \approx \frac{T_{\mathrm{CW}}}{A+\log(J_{||}/J')}$ was not shown in the Mermin-Wagner's 1966 PRL paper which is one of pioneering works on ordering physics in low dimensions. Built upon the foundation provided by the Mermin-Wagner's 1966 PRL paper, this equation was introduced later and widely used in many studies of low-dimensional magnetism afterwards, for example, *J. Mag. Mag. Mater. 1989, 82, 294-296* by Liu, *Phys. Stat. Sol. B 1993, 175, 237* by Wei and Du, *Phys. Rev. Lett*. 2005, 94, 217201 by Yasuda, Todo, Hukushima, *et al,* and inexplicitly in *Phys*. *Rev*. *Lett*. 1988, 60, 1057 by Chakravarty, Halperin and Nelson.

Action taken: We updated the only two places in the main text where we called "Mermin-Wagner" to ".... the stronger ~~Mermin-Wagner~~ fluctuations expected at the surface, we refer to the ~~Mermin-Wagner~~ formula, …" by removing "Mermin-Wagner" in Line 227. We also updated the references at "formula" to include the four references listed in the related paragraph.

7) Following up from my previous comments, the equation for T_N is a mean-field based equation which has several limitations on the consideration of exchange interactions, thermal effects, etc. In order to be convincing, proper micro-magnetic or atomistic simulations would need to be undertaken at different thickness, system sizes, etc. in order to elucidate any dependence of the transitions at the surface and inner bulk. The variation of T_CW, J_1,2,3 with the Hubbard-U parameter is really not convincing. This seems very adjusted to the system size to give the corresponding results, which seems artificial. The Hubbard-U might be dependent on the thickness of the system (e.g. 1L, 2L, ..) relative to bulk. However, once it is calculated for that particular thickness (via linear response, or Monte Carlo, etc.), and it should be constant, and not anymore tunable.

We understand and totally agree that there are multiple theoretical approaches to explain an experimental finding. Here, our experimental finding is that we revealed an additional onset temperature T_{S} = 140K in addition to the detection of the known bulk AFM onset at T_{N} = 132K and the previously assigned intermediate state temperature scale T^{**} = 155K in the high quality CrSBr single crystals. We assigned this onset at T_{S} = 140K to be the surface AFM transition temperature, based on our careful symmetry analysis. The goal of our theoretical calculations is to find an interpretation for this higher surface AFM transition temperature.

We would like to clarify that our calculations aim to check the relative amplitudes between surface and bulk magnetic critical temperatures (i.e., check T_S > or = or < T_N), rather than identifying the accurate values for them. In this context, varying the Hubbard U is used to confirm the consistency of the finding of $T_S > T_N$ which is **independent** of the Hubbard U value. That is to say, the calculated result is robust against the choice of Hubbard U.

It is true that we approximated the surface effect by three different scenarios of monolayer CrSBr (S2, S3, and S4 listed in the main text) to compare with the bulk (S1). Our first-principle calculations of the seven Heisenberg exchange coupling $J_{1\text{-}7}$ identify three of the seven, $J_{1\text{-}3}$, show significant responses to scenarios S1-4. Furthermore, their combined effect to increase T_{CW} (thus T_S) is maximized for S3, fixed *ab* monolayer CrSBr that is derived from the intra-unit cell structure relaxation while keeping the lattice constant same as the bulk. We further confirmed that the trends of T_{CW} and $J_{1\text{-}3}$ for S1-4 four scenarios are independent of the Hubbard U value.

From these calculated results, we gather that the increased onset temperature at the surface is likely due to the greater $J_{1\text{-}3}$ at the surface than in the bulk. This originates from the combination of 1) the intra-unit cell structural relaxation that enhances $J_{2\text{-}3}$, and 2) the suppression of a hopping pathway involving the neighboring layer that contributes an AFM intralayer exchange coupling to the FM $J_{1\text{-}2}$.

Thus, our model captures the essential physics for interpreting our experimental finding of $T_S > T_N$ in a consistent fashion, although it does not provide accurate values of T_N and T_S. We agree with Reviewer #2 that there could be other theoretical approaches, such as micro-magnetic or atomistic simulations, that can provide more accurate values to reproduce the experimental results, which is definitely exciting and important – but they could be independent studies and are beyond the scope of this current work.

In summary, our first principles calculations not only verify $T_S > T_N$ for CrSBr, but also provide insight information of its origins.

Action taken: We added in Lines 248 – 251: "We vary the Hubbard U across a wide range to verify the consistent and robust trend of T_{CW} for the four scenarios: T_{CW} increases from the bulk to the rigid monolayer, further enhances in the fixed *ab* monolayer, but decreases a bit in the free monolayer, as shown in Fig. 6b."

8) Thermal fluctuations might happen at the surface as it is pointed out (page 6), but they tend to thermalise and consequently dying out with time. If the system is not in equilibrium initially, it would be very hard to measure any property thermodynamically speaking. So, this argument to explain the increase in the magnetic onset temperature at the surface seems not the case here.

If we understand correctly this question from Reviewer #2, his/her concern is that a time-dependent temperature variation (the "thermal fluctuation" that Reviewer #2 refers to) may happen at the surface and could lead to improper experimental measurements. We would like to approach this question in three steps.

1. From our understanding, thermal fluctuations describe random deviations of a material system from its average state, which occur in systems **at equilibrium** and are caused **by finite**

temperature (T > 0K) [See reference: *Landau, L. D. and Lifshitz, E. M. Statistical Physics. Pergamon Press, 1993.*]. For example, in the layered AFM phase of 3D CrSBr (0K < T < T_N), the average state is the left/right/left/right… or right/left/right/left… spin arrangement across the layers ("left" and "right" refer to spin along the positive and negative direction along the *b*-axis). Thermal fluctuations refer to the random, slight canting of spins at individual Cr sites to deviate from the "left" or "right" direction that is activated by the thermal energy at any finite, constant temperature.

2. Thermal fluctuations are known to be stronger in 2D than in 3D because of the reduction of neighbors in the real space in 2D as compared to 3D, for a same material (2D CrSBr vs 3D CrSBr) at the same temperature. Using this knowledge, we consider the surface of 3D CrSBr has fewer neighbors than the inner bulk of 3D CrSBr, and therefore, expect stronger thermal fluctuations to happen at the surface than in the inner bulk of 3D CrSBr.

   From point 1, thermal fluctuations make the system deviate from the order. That is to say, the stronger the thermal fluctuations are, the harder the order can form. Following this argument, one would naturally and intuitively expect a lower magnetic onset temperature at the surface than in the bulk. However, our results show the **opposite**: the surface has a higher magnetic onset than the bulk, which is counter-intuitive and interesting.

3. Our RA SHG technique, which captures the 140K surface onset, is a probe of the ground state in equilibrium at finite temperatures. For the measurements at every temperature, we wait for additional 5 minutes to stabilize the temperature, after the temperature reach the set point through a slow heating/cooling rate of 0.5K/minute. This ensures the sample as a whole, including the surface and the inner bulk, reaches and maintains at the setpoint temperatures during our data acquisition. Furthermore, we can also prove the stability of our system by showing the consistency of RA SHG data taken at the same temperature but 45 minutes apart. Figure R13 shows four RA SHG patterns taken every 15 min in the P_{in}-P_{out} channel at 130K. Within our technique sensitivity, there are no observable changes in the measured patterns, indicating the system is in its equilibrium state.

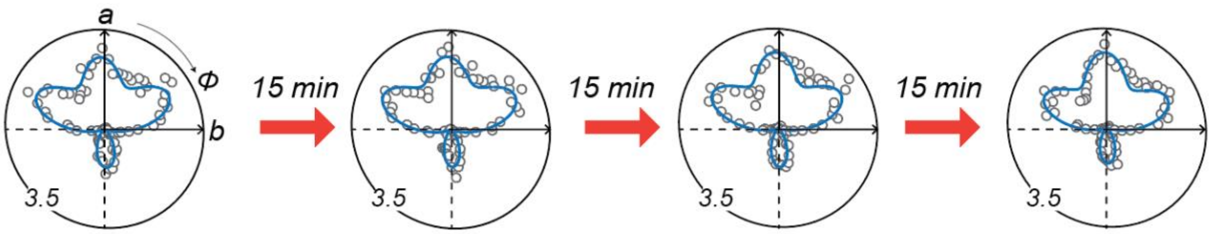

Figure R13 | SHG RA patterns taken every 15 min in the P_{in}-P_{out} channel at 130K. No observable changes are detected, indicating the system is in its equilibrium state.

In summary, our system is at equilibrium, and our measurements probe the equilibrate properties of 3D CrSBr. The observed 140K onset for the surface AFM order, which is higher than the 132K bulk AFM onset temperature, is an intrinsic, thermodynamic property of 3D CrSBr.

Action taken: We have provided the details of the heating/cooling rate and the temperature stabilization procedure in the Method section. We added in Lines 159 – 162: "During SHG measurements, we ensure our system is in thermal equilibrium by keeping a slow heating rate, waiting for additional time after the temperature is stabilized (see Methods), and noticing no SHG pattern change as a function of time (see Supplementary Materials Section 8 for SHG RA patterns measured in sequence of time)."

We further added the RA SHG data taken at the same temperature but separated time in Supplementary Materials Section 8.

9) The paper is very confusing in the way the different types of potential transitions occurred at finite system, the first paragraph would need a full re-writing, and the definitions reviewed.

Action taken: we rewrite the first paragraph as follows:

> "Surfaces are always present in practical materials. Even in macroscopic materials, the presence of surfaces has the potential to enrich their phase diagrams of spontaneous symmetry breaking phases[1-4]. Taking magnets as an example, in the temperature (T) versus surface-to-bulk relative exchange interaction (J_s/J_b) phase diagram shown in Fig. 1a, three distinct phase transitions were theoretically identified, namely "ordinary", "surface", and "extraordinary" transitions. The typical transition, where the surface and the bulk order simultaneously, is called "ordinary", and the one when the surface orders, but the bulk does not, is a "surface" transition. The transition establishing the bulk order in the presence of the surface order is called "extraordinary". The point where three different phases meet is a "special point". In the "ordinary" case when J_s is weaker than J_b, the bulk order generates an effective field to induce a finite order at the surface, and thus the system undergoes only a single phase transition. Conversely, in the "surface" and "extraordinary" cases with J_s greater than J_b, the surface order cannot provide a notable effective field deep in the inner bulk, and thus, the bulk undergoes a separate "extraordinary" phase transition, leading to the split into two phase transitions."

Finally, we express our gratitude to Reviewer #2 for conducting a thorough examination of our manuscript and providing valuable suggestions for its enhancement. In this revision, we hope to address Reviewer #2's inquiries through our thorough characterization of our sample quality, faithful reproduction of our key findings of split surface and bulk magnetic transitions, detailed description of our experiment procedures, and in-depth validation of our mean-field model and DFT calculations. Once again, we extend our appreciation to Reviewer #2 for their insightful evaluation of our manuscript.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have included a thorough response and revision of the manuscript, including new measurements to resolve the sample-dependence issue. With these revisions, their paper is much more compelling. I personally remain skeptical that their observation is indeed a surface ordering, but the authors have done an admirable job in making a reasonable case.

Therefore, I will recommend publication in Nature Communications, provided the second referee also endorses.

Reviewer #2 (Remarks to the Author):

I have reviewed again the paper by Guo et all. and their response to their reviewer's questions. I still have concerns that preventing the acceptance of this paper. In particular:

1) As I mentioned in my previous comments, CrSBr is a biaxial anisotropy material with a well defined spin Hamiltonian as described in Appl. Phys. Lett. 117, 083102 (2020) and New J Phys 25, 013026 (2023). The non-inclusion of the right interactions in the model would inevitably overlooked any effect present, in particular those where the surface properties need to be separated from the bulk ones. In this aspect, the mean field arguments included in the response looked very limited or hand-waving.

Normally, there is a big difference between calculation of exchange interactions from DFT, and the real computation of TN or Tc from atomistic or micro magnetic methods. That is, not necessarily the values of the exchange interactions individually analysed, as it is done in the manuscript, might provide a good explanation of the effect. The main aspect is on the cooperative aspect of the interactions playing all together. A good start point is to reproduce the M vs. T curve and its peculiar transitions observed in the experiments using their Heisenberg model, and calculated exchange interactions. With this information, we would know whether this approach is convenient or not. The discussions of how individual terms (e.g. anisotropy, J_||, etc.) may affect TN looks very approximated without any quantitative results in terms of Monte Carlo simulations, or something close to it.

2) Following up previous point, there is a large difference between the interlayer exchange interactions and interlayer ones. For instance, if you look at New J Phys 25, 013026 (2023), the difference persists in both bulk and few-layers without apparent modifications. Similar results for bulk has been measured via neutron experiments (Ref. 23). So, I don't understand the diagram in Figure 1 for 2D, which states J_|| >> J_perp. This doesn't look very accurate though.

3) About the variation of the Hubbard U term, no, it is not the case. If the Hubbard U is varied, the values of the magnetic parameters (exchange interactions, anisotropies, DMI, etc.) would inevitably change as it is showed in Figure 6. There are a few cases however that the increment of one parameter, may be compensated by the reduction of another, which in the end may end up in a non-dependence of the transition temperatures on the value of the Hubbard U. So, the argument to say that the "….TS > TN which is independent of the Hubbard U value" is not convinced without simulations proving it. If the authors had done a systematic study in terms of micro-magnetic simulations this would be easily clarified.

4) It still remains the problem to separate the contributions from bulk and surface on the effect. I noticed the estimation of the penetration depth for the light used in the measurements of 450 nm. Figure R1 also helps to provide some insights in this issue, but it's not clear whether the reduction of sample volume in thinner systems, or the surface itself, is the leading contribution to the SHG signal. Since three samples were used in Figure R1 (160 nm, 450 nm, 7.5 micro-meter) but at 80 K, which is below the surface transition (140 K). If the authors want to be convincing, they may consider to extract the signal at 140 K and 132 K (bulk order) at those thicknesses. Then, we would know how sensitive SHG is to the subtle magnetic transitions in CrSBr. At the moment, it is not clear.

5) On the diagrams in Figure 5e-5g, why to define the surface layers as only 3 layers? Why not 4 or 5 layers instead? Do you have any exp data or simulations supporting the idea that the separation between surface and bulk occurred at that thickness or determined range? It looks very arbitrary without any solid evidence of this argument, and more a sketch than a real result. I'd suggest the authors to remove the panels 5e-5g, and if possible, include real simulations at least providing some insights.

Point-by-point response to the review report.

We are happy to learn that Reviewer #1 is satisfied with our revision and does not have further questions in this round of review. We thank his/her effort in reviewing our manuscript.

Reviewer #2 (Remarks to the Author):

I have reviewed again the paper by Guo et all. and their response to their reviewer's questions. I still have concerns that preventing the acceptance of this paper. In particular:

1) As I mentioned in my previous comments, CrSBr is a biaxial anisotropy material with a well defined spin Hamiltonian as described in Appl. Phys. Lett. 117, 083102 (2020) and New J Phys 25, 013026 (2023). The non-inclusion of the right interactions in the model would inevitably overlooked any effect present, in particular those where the surface properties need to be separated from the bulk ones. In this aspect, the mean field arguments included in the response looked very limited or hand-waving.

Normally, there is a big difference between calculation of exchange interactions from DFT, and the real computation of TN or Tc from atomistic or micro magnetic methods. That is, not necessarily the values of the exchange interactions individually analysed, as it is done in the manuscript, might provide a good explanation of the effect. The main aspect is on the cooperative aspect of the interactions playing all together. A good start point is to reproduce the M vs. T curve and its peculiar transitions observed in the experiments using their Heisenberg model, and calculated exchange interactions. With this information, we would know whether this approach is convenient or not. The discussions of how individual terms (e.g. anisotropy, J_||, etc.) may affect TN looks very approximated without any quantitative results in terms of Monte Carlo simulations, or something close to it.

We are aware of the biaxial anisotropy present in CrSBr, as Reviewer #2 pointed out. Moreover, we note that the literature cited by Reviewer #2, *Appl. Phys. Lett. 117, 083102 (2020)* and *New J Phys 25, 013026 (2023)*, explicitly calculated to show that in CrSBr, the biaxial anisotropy is 2-3 orders of magnitude smaller than the intralayer exchange coupling. The smallness of the biaxial anisotropy is also corroborated experimentally by the small spin wave gap in *Nature 609, 282 (2022)* and *Adv. Sci. 9, 2202467 (2022)*.

More importantly, as we explained in the main text and the last round of revision, all the anisotropy terms enter the expression for T_N under a logarithm, while the intralayer exchange enters linearly. As a result, T_N is determined by the intralayer exchange coupling, which is well documented in literature [*J. Mag. Mag. Mater. 82, 294 (1989), Phys. Stat. Sol. B 175, 237 (1993), Phys. Rev. Lett. 94, 217201 (2005)*, *etc.* that we have cited].

To the suggestion on Monte Carlo simulations:

Monte Carlo simulations of Mermin-Wagner systems is well-known to be a formidable task because of logarithmic dependence on the system size, and only a handful papers in the literature thus far have managed to achieve this (see *J. Magn. Magn. Mater. 262, 316 (2003)*, *Phys. Rev. Lett. 94, 217201 (2005)*) Existing literature of Monte Carlo simulations of CrSBr, e.g. *Phys. Rev.*

B 104, 144416 (2021), shows that calculated transition temperature is clearly different from the experimental result.

We would like to note that the calculations of exact transition temperatures of 3D CrSBr have never been our aim. Our goal was to establish the trend of the transition temperatures between the bulk and the surface magnetism in 3D CrSBr, but not their individual values. In this regard, we think the Monte Carlo simulations for 3D CrSBr are not only unfeasible but also unnecessary.

Action Taken: We are now citing both references cited by the referee, *Appl. Phys. Lett. 117, 083102 (2020)* and *New J Phys 25, 013026 (2023)*, since they are consistent with our claim of the smallness and irrelevance of biaxial anisotropies in CrSBr and show their logarithmically small impact on T_{N}.

2) Following up previous point, there is a large difference between the interlayer exchange interactions and interlayer ones. For instance, if you look at New J Phys 25, 013026 (2023), the difference persists in both bulk and few-layers without apparent modifications. Similar results for bulk has been measured via neutron experiments (Ref. 23). So, I don't understand the diagram in Figure 1 for 2D, which states J_|| >> J_perp. This doesn't look very accurate though.

We assume that the referee meant "*between interlayer* ($J_\perp$) *and intralayer* ($J_{||}$)". If so, our assessment of $J_{||} \gg J_\perp$ is completely consistent with Ref. 23 and with *New J Phys 25, 013026 (2023)*, both of which find that $\mathrm{J}_{||} \gg \mathrm{J}_\perp$ by four orders of magnitude.

Action Taken: To avoid any possible confusion, we now define explicitly that $J_{||}$ stands for the intralayer exchange coupling and $J_\perp$ for the interlayer coupling in our main text.

3) About the variation of the Hubbard U term, no, it is not the case. If the Hubbard U is varied, the values of the magnetic parameters (exchange interactions, anisotropies, DMI, etc.) would inevitably change as it is showed in Figure 6. There are a few cases however that the increment of one parameter, may be compensated by the reduction of another, which in the end may end up in a non-dependence of the transition temperatures on the value of the Hubbard U. So, the argument to say that the "….TS > TN which is independent of the Hubbard U value" is not convinced without simulations proving it. If the authors had done a systematic study in terms of micro-magnetic simulations this would be easily clarified.

We first clarify our purpose of varying U: Because the exact value of U is not known, we vary U to show that our conclusions hold for any reasonable U.

As explained above and in the previous round, anisotropies, including the anisotropic exchange, DMI, etc., all enter the expression of T_{N} under a logarithm and are therefore hardly important. As a result, the intralayer Heisenberg couplings are the main important parameters in determining T_{N}, whose trend across the four cases remain consistent upon varying U.

To the suggestion on micro-magnetic simulations:

Micromagnetic simulations are continuum models to describe magnetic properties at sub-micrometer length scales. It is not clear to us how such models can help explain the enhanced T_{N}

at the surface of 3D CrSBr. Perhaps Reviewer #2 meant “microscopic simulations” such as Monte Carlo simulations? However, as explained above, Monte Carlo simulations for Mermin-Wagner systems are neither feasible nor necessary.

4) It still remains the problem to separate the contributions from bulk and surface on the effect. I noticed the estimation of the penetration depth for the light used in the measurements of 450 nm. Figure R1 also helps to provide some insights in this issue, but it’s not clear whether the reduction of sample volume in thinner systems, or the surface itself, is the leading contribution to the SHG signal. Since three samples were used in Figure R1 (160 nm, 450 nm, 7.5 micro-meter) but at 80 K, which is below the surface transition (140 K). If the authors want to be convincing, they may consider to extract the signal at 140 K and 132 K (bulk order) at those thicknesses. Then, we would know how sensitive SHG is to the subtle magnetic transitions in CrSBr. At the moment, it is not clear.

The primary principle to separate the surface and bulk contributions in this current work is to rely on their distinct point group symmetries. Luckily, in 3D CrSBr, the surface magnetic point group (m’m2’) and the bulk magnetic point group (mmm1') are different, which give distinct polarization dependent SHG responses. We have provided the detailed analysis in our previous round of review report (~3 pages description), showing that we can reliably decouple the surface and bulk contributions. This analysis process was included in Supplementary Materials section 6. The thickness dependence is only a secondary check.

To the suggestion on “extract the signal at 140 K and 132 K (bulk order) at those thicknesses”:

This is unfortunately unfeasible here. Both the surface and bulk magnetic orders go through second-order phase transitions. Right at their critical temperatures, their order parameters remain as zero and hence have no contributions to the SHG signal.

Action Taken: We have made it clear in Supplementary Materials section 7 that the symmetry analysis is the primary criterion to distinguish the surface and bulk contributions to SHG whereas the thickness dependence is a secondary check.

5) On the diagrams in Figure 5e-5g, why to define the surface layers as only 3 layers? Why not 4 or 5 layers instead? Do you have any exp data or simulations supporting the idea that the separation between surface and bulk occurred at that thickness or determined range? It looks very arbitrary without any solid evidence of this argument, and more a sketch than a real result. I’d suggest the authors to remove the panels 5e-5g, and if possible, include real simulations at least providing some insights.

We intended to use the cartoon illustration to show the multiple stages of the magnetic phase transitions. And we agree that the cartoon illustration does not contain quantitative information in terms of the lateral dimensions and the separation between “surface” and “bulk”.

We took Reviewer #2’s suggestion and removed this cartoon illustration.

Action Taken: We have removed the cartoon illustration in Figure 5 and the associated text.

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

I reviewed again this manuscript altogether with the SI and rebuttal letter. The authors have not addressed any of my comments on the simulation and experimental sides with solid evidence and/or data that demonstrated the validity of their arguments. They justified their points with published papers in the literature which don't remarks any of the open questions still present in the manuscript.

I have to say that over the rebuttal letter, I counted the word 'unfeasible' and 'unnecessary' twice each, which seems the authors are not very on the side to address my comments but rather have the paper accepted without any further modification or in-depth analysis. We are probably on the 3rd round of revisions but none of my comments have yet been properly addressed. Thus, I cannot recommend this manuscript for publication in this journal.

On a more technical side:

1) The Hamiltonian used at the end of the paper without any anisotropic terms would be applicable only in the limit of a zero-anisotropy compound, which is clearly not the case for CrSBr. The readers/community will see this and promptly they will see that something isn't right on the physical description of the interactions on this magnetic. Thus, the authors should realise that isn't this referee trying to turn down the paper, but it is the information/data already included doing so.

2) I read carefully the SI Section 6, 7 and the results included. We may see on Figure S8 how the bulk SHG signal starts contributing as the thickness increases (e.g. 450 nm), however, the surface signal (m'm2') is pretty much the same despite of the thickness. With a penetration depth of ~450 nm, it would be unlikely to clearly separate both contributions. This means that we would know when a more volumetric contribution coming from the bulk might take place because the thickness is showing that. However, we don't know when the surface transition would be present. A much smaller penetration depth would be required though.

3) On the Hubbard U, I am not convinced with the discussions included. Generally one of the best way to quantify the right Hubbard U and the exchange term J for a given system is via linear-response theory which is already implemented in the ab initio software used in the manuscript. I am

surprised that the authors haven’t not done so, but rather varied the magnetic parameters as a function of U instead.

Reviewer #3 (Remarks to the Author):

The authors investigate the phase transition of bulk CrSBr by means of second harmonic generation. By distinguishing between electric dipole contributions (at the surface) and electric quadrupole contributions (from the bulk) they are able to demonstrate the existence of a surface magnetic order above the bulk Neel temperature. The results seem to resolve previous discrepancies regarding the critical temperature n this materials and is in good agreement with the fact that thinner samples exhibit higher transition temperatures. The tries to rationalise the results using first principles calculations and mean field theory. Due to the strong current interest in 2D and vdW magnetism I believe that a large community will find the work interesting and I recommend it for publication in Nature Communications. I do have a few comments that the authors may consider:

The theoretical treatment based on DFT is a little bit shaky it seems. The authors argue that calculated exchange constants are increased in the surface relative to bulk. But in reality they only compare exchange constants for bulk and a monolayer. It is not completely obvious that the monolayer calculations are representative of the surface. Also the relaxation could be rather sentive to, which functional is applied. It is nicely demonstrated that the trend is conserved with PBE+U, but what about vdW interactions, which certainly plays a role in bulk?

The presentation of the DFT results in the main manuscript (lines 251-265) is a bit unclear. Instead of going into a (little boring) discussion on which exchange constant does what in this and that scenario, I would suggest the authors to simple state the expression for the T_CW and discuss the role of this quantity as a descriptor that correlates with T_N rather than an actual estimate of the critical temperature and state the values for T_CW obtained for bulk ab-fixed and rigid monolayers. The author may also consider mentioning that the Neel temperature of a 2D layer can only be non-vanishing as a consequence of anisotropy - seems relevant when an isotropic model Hamiltonian is chosen.

The authors mention that Neutron diffraction on powder found a critical tmeperature of 140 K, which represents the onset of surface order. Can that really be true? Could the authors estimate the ratio of surface to bulk in such powder samples? I would expect that to be small - even for powder samples.

In lines 177 the contributions from the surface (ED) and bulk (EQ) is described and the results of the signals are shown in Fig. 5b and 5c. However, in 5C there is a clear peak at T_S although that signal is supposed to describe the bulk EQ. I think this needs to be explained better.

Minor comment: Line 61 it is written that the onset of AFM order for a monolayer is 146 K. I suppose that should just be ferromagnetic order in the case of a monolayer?

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

I reviewed again this manuscript altogether with the SI and rebuttal letter. The authors have not addressed any of my comments on the simulation and experimental sides with solid evidence and/or data that demonstrated the validity of their arguments. They justified their points with published papers in the literature which don't remarks any of the open questions still present in the manuscript.

I have to say that over the rebuttal letter, I counted the word 'unfeasible' and 'unnecessary' twice each, which seems the authors are not very on the side to address my comments

We thank Reviewer 2 for their time and effort in reviewing our work. We have considered their comments carefully and tried our best to implement them wherever applicable.

On a more technical side:

1) The Hamiltonian used at the end of the paper without any anisotropic terms would be applicable only in the limit of a zero-anisotropy compound, which is clearly not the case for CrSBr. The readers/community will see this and promptly they will see that something isn't right on the physical description of the interactions on this magnetic. Thus, the authors should realise that isn't this referee trying to turn down the paper, but it is the information/data already included doing so.

We always agree that the spin Hamiltonian in CrSBr has the biaxial anisotropy term, and at the same time, we consistently point out that the biaxial anisotropy term cannot explain the enhanced T_N, as its change does not affect T_N in any appreciable way. It is the intralayer exchange term that primarily contributes to the enhancement in T_N. Let's start by the expression for T_N, $T_N \approx \frac{T_{CW}}{A+\log(J_{||}/J')}$, where

$$T_{CW} = -\frac{1}{3}S(S+1)(2J_1 + 4J_2 + 2J_3 + 4J_4 + 4J_5 + 2J_6 + 4J_7)$$

We can clearly see that the change in intralayer exchange coupling (J_{1-7}) will impact T_N in a linearly proportional scale, whereas the change in the biaxial anisotropy (included in J') would influence T_N in a logarithmical scale – a much smaller scale than the linear scale. We did the numerical estimation in our first round of report to Question 5) of Reviewer #2 to illustrate this point.

In other words, intralayer exchange coupling and biaxial anisotropy are both present and could change between deep bulk and surface. However, for the same percentage of change in these two parameters, the leading order contribution to the change in T_N is the change in intralayer exchange coupling. We have done the calculations to evaluate the change in intralayer exchange coupling between bulk and surfaces, and confirmed their enhancement at the surface that convincingly explains the enhancement of T_N.

When and only when the leading order contribution fails to explain our results (which is not the case here) do we need to move on to the next order contributions, for example, the change in the anisotropy term.

Action taken: we clarified further in Line 237-241: "From Eq. (1) and Eq. (2), we can see that the change in intralayer exchange coupling (J_{1-7}) will impact T_N on a linear scale whereas the change in the intralayer anisotropy and interlayer coupling (included in J') will influence T_N on a logarithmical scale. Thus, the leading order contribution to the enhanced T_N at the surface should be the change in the intralayer exchange coupling from bulk to surface."

2) I read carefully the SI Section 6, 7 and the results included. We may see on Figure S8 how the bulk SHG signal starts contributing as the thickness increases (e.g. 450 nm), however, the surface signal (m'm2') is pretty much the same despite of the thickness. With a penetration depth of ~450 nm, it would be unlikely to clearly separate both contributions. This means that we would know when a more volumetric contribution coming from the bulk might take place because the thickness is showing that. However, we don't know when the surface transition would be present. A much smaller penetration depth would be required though.

Comparing the RA SHG data between 160 nm and 450 nm CrSBr, the ED contribution under *m'm2'* remains nearly the same (as Reviewer #2 observed), but the EQ contribution under *mmm1'* is visibly increased. This is exactly consistent with our assignment of ED contribution that is from the surface (depth shallower than 160 nm) and EQ contribution that is from the bulk (depth deeper than 160 nm), based on our symmetry analysis.

Based on the experimental results from samples of discrete thicknesses, we cannot precisely specify what the depths are for the surface and bulk. However, it is not the focus of this work to quantify the depths of surface and bulk, because the separation between them is done reliably by their distinct symmetries, as we explained in detail in previous responses and in the Supplementary Information.

3) On the Hubbard U, I am not convinced with the discussions included. Generally one of the best way to quantify the right Hubbard U and the exchange term J for a given system is via linear-response theory which is already implemented in the ab initio software used in the manuscript. I am surprised that the authors haven't not done so, but rather varied the magnetic parameters as a function of U instead.

Tuning Hubbard U over a relatively wide range is to verify the robustness and consistency of the trend of enhanced T_{CW} (and hence T_N) at the surface, which is the key purpose of the theoretical calculations. We find this way is more reliable and useful than choosing one single estimated U, for the following reason. It is generally known and accepted that there is no good way to calculate U, and to the best, one can only get a reasonable estimate of U on the ballpark using various computational methods (including the linear response theory in the ab initio software we used). Given that our goal is to explain the enhanced T_N at the surface, rather than provide the precise value of T_N, choosing a range of U to show the consistency of the enhanced trend is therefore more reasonable.

Reviewer #3 (Remarks to the Author):

The authors investigate the phase transition of bulk CrSBr by means of second harmonic generation. By distinguishing between electric dipole contributions (at the surface) and electric quadrupole contributions (from the bulk) they are able to demonstrate the existence of a surface magnetic order above the bulk Neel temperature. The results seem to resolve previous discrepancies regarding the critical temperature n this materials and is in good agreement with the fact that thinner samples exhibit higher transition temperatures. The tries to rationalise the results using first principles calculations and mean field theory. Due to the strong current interest in 2D and vdW magnetism I believe that a large community will find the work interesting and I recommend it for publication in Nature Communications. I do have a few comments that the authors may consider:

We sincerely thank Reviewer #3 for carefully reading our manuscript and assessing our work positively. Below, we provide a point-to-point response to the reviewer's questions.

The theoretical treatment based on DFT is a little bit shaky it seems. The authors argue that calculated exchange constants are increased in the surface relative to bulk. But in reality they only compare exchange constants for bulk and a monolayer. It is not completely obvious that the monolayer calculations are representative of the surface. Also the relaxation could be rather sentive to, which functional is applied. It is nicely demonstrated that the trend is conserved with PBE+U, but what about vdW interactions, which certainly plays a role in bulk?

We also recognize the difference between the surface and the monolayer CrSBr. Because of this, we choose to simulate three different cases for the monolayer CrSBr (S2-S4). Among these three cases, it is S3 that shows the greatest enhancement in T_{CW}, and it is also S3 that mimics a CrSBr flake at the surface of 3D CrSBr – allows intra-unit cell relaxation while keeping the atomic constant same as the bulk CrSBr. Hence, we believe that the major contributions to the enhanced T_{CW} (and hence T_{N}) at the surface are revealed: (1) the missing neighboring layer and (2) the intra-unit cell relaxation, even if S3 is not fully representative to the surface of 3D CrSBr.

The reviewer's comment on the vdW interactions is important and insightful. In all our calculations we used one of the latest prescriptions for this correction, the non-local optB88-vdW functional of Klimeš et al [J. Klimeš, D. R. Bowler, and A. Michaelides, J. Phys.: Condens. Matter 22, 022201 (2010)]. We should have mentioned this information in our earlier version.

Action taken: we have added this information to the Methods section.

The presentation of the DFT results in the main manuscript (lines 251-265) is a bit unclear. Instead of going into a (little boring) discussion on which exchange constant does what in this and that scenario, I would suggest the authors to simple state the expression for the T_CW and discuss the role of this quantity as a descriptor that correlates with T_N rather than an actual estimate of the critical temperature and state the values for T_CW obtained for bulk ab-fixed and rigid monolayers. The author may also consider mentioning that the Neel temperature of a 2D layer can only be non-vanishing as a consequence of anisotropy - seems relevant when an isotropic model Hamiltonian is chosen.

We thank the reviewer for their helpful suggestions. We improved the presentation accordingly in the revised version.

Action taken: we have changed Line 226-241 to: “To understand the increase in the surface magnetism onset temperature in CrSBr despite the stronger fluctuations expected at the surface, we refer to the formula[44-47]:

$$T_{\mathrm{N}} \approx \frac{T_{\mathrm{CW}}}{A + \log\left(J_{||}/J^{'}\right)}. \tag{1}$$

Here, T_{CW} denotes the mean-field Curie-Weiss temperature for monolayer CrSBr; A is a constant of the order of 3-5; $J_{||}$ is the average characteristic intralayer exchange coupling; $J^{'}$ represents a properly-defined combination of the interlayer coupling $J_{\perp}$ and the intralayer anisotropy D, which arises from both the single site anisotropy and the Ising exchange – in a previous study[48], $J^{'}$ was estimated as $J^{'} = D + J_{\perp} + \sqrt{(D + J_{\perp})^2 - D^2}$. Note that it is the small but nonzero intralayer anisotropy D that maintains T_{N} finite for monolayer CrSBr[21,24]. Within the mean-field theory, T_{CW} is directly related to the intralayer exchange coupling strengths:

$$T_{CW} = -\frac{1}{3}S(S+1)(2J_1 + 4J_2 + 2J_3 + 4J_4 + 4J_5 + 2J_6 + 4J_7) \tag{2}$$

where $S = 3/2$ and J_{1-7} are the intralayer exchange couplings up to the 7th nearest neighbor. From Eq. (1) and Eq. (2), we can see that the change in intralayer exchange coupling ($J_{1\text{-}7}$) will impact T_{N} on a linear scale whereas the change in the intralayer anisotropy and interlayer coupling (included in J') will influence T_{N} on a logarithmical scale. Thus, the leading order contribution to the enhanced T_{N} at surface should be the change in the intralayer exchange coupling from bulk to surface.”

Added to Line 255-258: “This observed trend suggests two important factors that lead to the increase of T_{CW}: first, the absence of neighboring layers, and second, the intra-unit cell lattice relaxation. Following Eq. (1), both factors will contribute to the enhanced T_{N} at the surface of CrSBr.”

The authors mention that Neutron diffraction on powder found a critical tmeperature of 140 K, which represents the onset of surface order. Can that really be true? Could the authors estimate the ratio of surface to bulk in such powder samples? I would expect that to be small - even for powder samples.

We thank Reviewer #3 for sharing this thought. And after careful consideration, we agree that we should be more cautious in interpreting the neutron powder diffraction data. One would need to know the powder size and the “surface” depth accurately to make the statement. We have revised our statement in the main text.

Action taken: in Line 207-209 of the main text, we revised the text to “the surface-to-bulk ratio is significantly increased from that of single crystal CrSBr, and thus, it might be possible that the powder neutron diffraction is sensitive to the surface magnetism”.

In lines 177 the contributions from the surface (ED) and bulk (EQ) is described and the results of the signals are shown in Fig. 5b and 5c. However, in 5C there is a clear peak at T_S although that signal is supposed to describe the bulk EQ. I think this needs to be explained better.

We thank Reviewer #3 for pointing out this observation. Below is our understanding about the weak peak at T_S in EQ SHG. ED SHG directly probes the surface Néel vector ($\mathbf{N}$) and is sensitive to CrSBr within the depth where the broken inversion symmetry at the surface extends to. EQ SHG, however, probes the spin correlations (i.e., $\mathbf{N} \cdot \mathbf{N}$) and is contributed by the CrSBr with the thickness of the light penetration depth (this includes and is beyond the surface depth that ED SHG is sensitive to). As a result, EQ SHG shows a weak divergent behavior when the surface magnetism orders and the spin correlations diverge.

Action taken: in Line 199-201, we added: "Note that EQ SHG probes CrSBr within the light penetration depth, which includes and goes beyond the surface depth. Provided its sensitivity to the spin correlation via the term $\mathbf{N} \cdot \mathbf{N}$, it shows a weak divergence, i.e., the peak, at T_S, as well as the slope change across T^{**}."

Minor comment: Line 61 it is written that the onset of AFM order for a monolayer is 146 K. I suppose that should just be ferromagnetic order in the case of a monolayer?

We thank the reviewer for pointing this out and we have corrected it in the manuscript.

Action taken: in Line 62, we changed the main text to "…140 K for bilayer CrSBr and the FM order onsets at possibly 146 K for monolayer CrSBr."