Supporting Information

Phonon Anharmonicity in Bulk T_d-MoTe2

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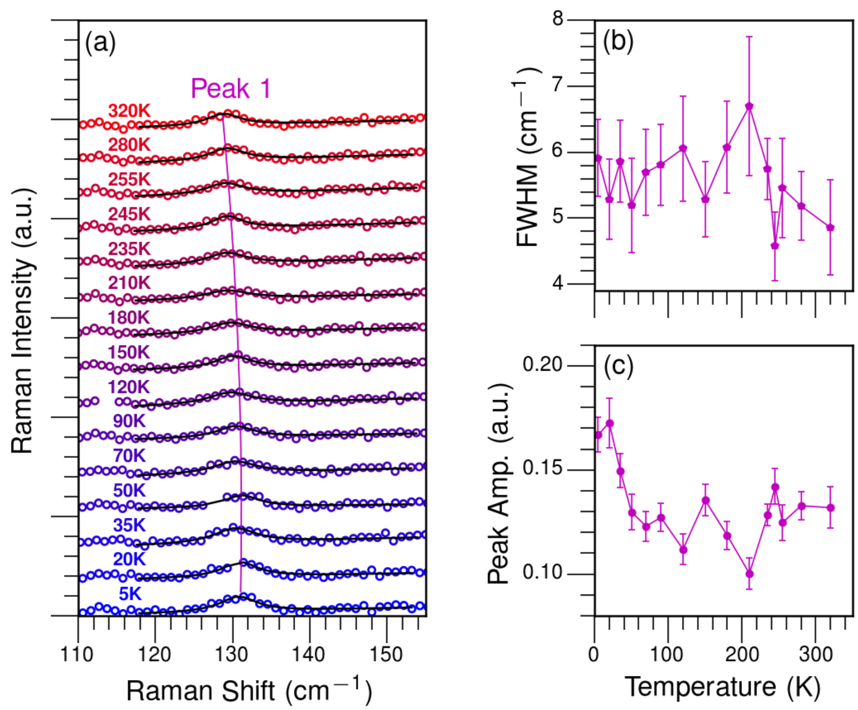

Figure S1 a) Temperature-dependent Raman spectra for Peak 1 normalized by the intensity of Peak 2 as labelled in Figure 1c. Solid black lines represent single Lorentzian fits with a linear background. b) FWHM of Peak 1 extracted from the fits at each temperature. c) Amplitudes of Peak 1, extracted from the fits in (a). 1σ error bars are included.

Raman Mode Assignment

Raman experiments in a backscattering geometry are sensitive to modes with A_g and B_g symmetry for the *1T'* phase and with A_1 and B_1 symmetries in the T_d phase.[1] In polarization-dependent Raman measurements of *1T'*-$MoTe_2$, which will be reported elsewhere, we have determined that Peaks 1-4 are of A_g symmetry. We now argue that these A_g modes evolve into A_1 modes in T_d-$MoTe_2$ based upon the similarity of their Raman tensors. The tensors for A_g and A_1 symmetry Raman modes are[1]

$$\overleftrightarrow{R}_{A_g} = \begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix} \qquad \overleftrightarrow{R}_{A_1} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}. \tag{S1}$$

The Raman cross-section S can be calculated from[2]

$$S = \left|\hat{e_s} \cdot \overleftrightarrow{R} \cdot \hat{e_i}\right|^2 \tag{S2}$$

where $\hat{e_i}$ and $\hat{e_s}$ are unit vectors for the polarization of the incident and scattered photons. In our experiment the excitation and collection paths are collinear and perpendicular to the basal plane of $MoTe_2$ (a backscattering geometry). The laser is polarized at an arbitrary angle θ with respect to the a crystal axis and ϕ is the polarization angle of the scattered light with respect to the same axis. $\phi=\theta$ and $\phi=\theta+\frac{\pi}{2}$ correspond to parallel and perpendicular collection configuration respectively. Therefore,

$$\hat{e_i} = \begin{pmatrix}\sin\theta & 0 & \cos\theta\end{pmatrix}, \tag{S3}$$

$$\hat{e_s} = \begin{pmatrix}\sin\phi & 0 & \cos\phi\end{pmatrix}. \tag{S4}$$

We now evaluate Eq. S2 for A_g symmetry modes using Eq. S3 and Eq. S4

$$S_{A_g} = \left|\begin{pmatrix}\sin\phi & 0 & \cos\phi\end{pmatrix}\begin{pmatrix}a & d & 0\\ d & b & 0\\ 0 & 0 & c\end{pmatrix}\begin{pmatrix}\sin\theta\\ 0\\ \cos\theta\end{pmatrix}\right|^2 \tag{S5a}$$

$$= \left|\begin{pmatrix}\sin\phi & 0 & \cos\phi\end{pmatrix}\begin{pmatrix}a\sin\theta\\ d\sin\theta\\ c\cos\theta\end{pmatrix}\right|^2 \tag{S5b}$$

$$= |a\sin\theta\sin\phi + c\cos\theta\cos\phi|^2. \tag{S5c}$$

We can perform a similar calculation for the A_1 symmetry mode

$$S_{A_1} = \left|\begin{pmatrix}\sin\phi & 0 & \cos\phi\end{pmatrix}\begin{pmatrix}a & 0 & 0\\ 0 & b & 0\\ 0 & 0 & c\end{pmatrix}\begin{pmatrix}\sin\theta\\ 0\\ \cos\theta\end{pmatrix}\right|^2 \tag{S6a}$$

$$= \left|\begin{pmatrix}\sin\phi & 0 & \cos\phi\end{pmatrix}\begin{pmatrix}a\sin\theta\\ 0\\ c\cos\theta\end{pmatrix}\right|^2 \tag{S6b}$$

$$= |a\sin\theta\sin\phi + c\cos\theta\cos\phi|^2. \tag{S6c}$$

Equations S5c and S6c are identical which, when combined with the continuous evolution of each mode with temperature, suggests that A_g modes will evolve into A_1 modes at low temperature.

A similar analysis can be performed for the B_g and B_1 symmetry Raman tensors

$$\overleftrightarrow{R}_{B_g} = \begin{pmatrix}0 & 0 & f\\ 0 & 0 & g\\ f & g & 0\end{pmatrix} \qquad \overleftrightarrow{R}_{B_1} = \begin{pmatrix}0 & 0 & f\\ 0 & 0 & 0\\ f & 0 & 0\end{pmatrix}. \tag{S7}$$

Following the same approach, we find

$$S_{B_g} = \left| \begin{pmatrix} \sin\phi & 0 & \cos\phi \end{pmatrix} \begin{pmatrix} 0 & 0 & f \\ 0 & 0 & g \\ f & g & 0 \end{pmatrix} \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix} \right|^2 = |f|^2(\sin(\theta+\phi))^2, \quad \text{(S8)}$$

$$S_{B_1} = \left| \begin{pmatrix} \sin\phi & 0 & \cos\phi \end{pmatrix} \begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ f & 0 & 0 \end{pmatrix} \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix} \right|^2 = |f|^2(\sin(\theta+\phi)).^2 \quad \text{(S9)}$$

Equations S8 and S9 are identical which, when combined with the continuous evolution of this mode with temperature, suggests that B_g modes will evolve into B_1 modes at low temperature.

Supplementary References

[1] M.I. Aroyo, J.M. Perez-Mato, D. Orobengoa, E. Tasci, G. De La Flor, and A. Kirov, Bulg. Chem. Commun. **43**, 183 (2011).

[2] H.B. Ribeiro, M.A. Pimenta, C.J.S. De Matos, R.L. Moreira, A.S. Rodin, J.D. Zapata, E.A.T. De Souza, and A.H. Castro Neto, ACS Nano **9**, 4270 (2015).