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ROLE OF PHONONS IN STRUCTURAL PHASE TRANSITIONS OF TRANSITION METAL DICALCOGENIDES

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Abstract.— To study the lattice instability of 1T-TiSe₂, phonon dispersion curves are calculated as functions of temperature by taking into account the effective ion-ion interactions caused by electron-lattice interaction. From the standpoint of the softening of phonon frequency we conclude that one of the transverse modes at the L point freezes as the distortion at the phase transition.

1. Introduction.

Semimetallic 1T-TiSe₂ transforms at about 200 K into a 2a×2a×2c superlattice structure¹ that is described as the condensed state of one of the transverse phonons at the L point in the Brillouin zone ($L_1^-(1)$ mode). For the formation of the superlattice we have presented a theory^{2,3} which is based on the band-type Jahn-Teller mechanism, and we have emphasized the role of the electron-lattice interaction. For several lattice distortions described by wave vectors at the symmetry points in the Brillouin zone we have calculated the generalized electronic susceptibility χ , in which the wave number and mode dependences of the electron-lattice interaction are included. We used the electronic band obtained by the tight-binding fit to the Zunger and Freeman's band.⁴ We found that the decrease of the electronic energy due to lattice distortion is the largest for the $L_1^-(1)$ mode with an amplitude ratio of 3:1 for the Ti and Se displacements. This result is consistent with the observation by neutron diffraction.¹ However, since the phase transition would occur when the decrease of the electronic energy due to the distortion exceeds the increase of the lattice energy, the study of the lattice dynamics is necessary to discuss the phase transition in more detail. In this paper we study the lattice dynamics of 1T-TiSe₂ by taking account of the effective ion-ion interactions caused by the electron-lattice interaction. We calculate the phonon dispersion curves as functions of temperature and discuss the results in connection with the structural phase transition.

2. Effective ion-ion interaction caused by electron-lattice interaction.

By using the adiabatic approximation and by calculating the second order perturbation with respect to the electron-lattice interaction, the effective ion-ion interaction is obtained as

$$V_{\text{eff}} = \frac{1}{2} \sum_q \sum_{\mu, \nu} \sum_{\alpha, \beta} \chi^{\alpha\beta}(\mu\nu, q) u_{\mu}^{\alpha}(q) u_{\nu}^{\beta}(-q), \quad (1)$$

where α and β are Cartesian coordinates and $u_{\mu}^{\alpha}(q)$ denote the Fourier amplitude of the α -component of the displacement $u_{\ell\mu} (= \sqrt{m_{\mu}} \delta R_{\ell\mu})$ of the μ th atom in the ℓ th unit cell. $\chi^{\alpha\beta}(\mu\nu, q)$ in eq. (1) is as follows:

$$\chi^{\alpha\beta}(\mu\nu, q) = \sum_{n,k} \sum_{n'} \left\{ \frac{1}{E_{nk}^0 - E_{n'k-q}^0} g^{\mu\alpha}(nk, n'k-q, E_{nk}^0) [g^{\nu\beta}(nk, n'k-q, E_{nk}^0)]^* \right. \\ \left. + \frac{1}{E_{nk}^0 - E_{n'k+q}^0} g^{\nu\beta}(nk, n'k+q, E_{nk}^0) [g^{\mu\alpha}(nk, n'k+q, E_{nk}^0)]^* f(E_{nk}^0) \right\}, \quad (2)$$

where E_{nk}^0 etc. are the band energies of the undistorted lattice, n and n' specify the bands, $f(E_{nk}^0)$ is the Fermi distribution function and g is the coefficient of the electron-lattice interaction given by

$$g^{\mu\alpha}(nk, n'k-q, E_{nk}^0) = \xi^{\mu\alpha}(nk, n'k-q) - E_{nk}^0 \eta^{\mu\alpha}(nk, n'k-q). \quad (3)$$

$\xi^{\mu\alpha}$ and $\eta^{\mu\alpha}$ are obtained in forms that include the derivatives of two-center transfer and overlap integrals with respect to $u_{\ell\mu}^{\alpha}$.

We have calculated $\chi^{\alpha\beta}(\mu\nu, q)$ for $T=0, 500$, and 1000 K and for $q=0$ (Γ point), ΓA , ΓM , $\frac{1}{2}\Gamma M$, ΓL , and $\frac{1}{2}AL$. μ (or ν) = 0, 1, and 2 denote the Ti, Se1, and Se2 ions in the unit cell. We take the x -axis along the ΓM line, the y -axis perpendicular to the ΓM line in the c -plane, and the z -axis perpendicular to the c -plane. As for the derivatives of the overlap integrals (denoted as $(pd\pi)'$, etc.) and those of the transfer integrals ($t'(pd\pi)$, etc.), only $pd\pi$, $pp\sigma$, $pp\pi$ are taken into consideration, because only these mainly contribute to χ . For $(pd\pi)'$ etc. we use the values of $1/\sqrt{2}$ times those evaluated by using the Slater functions. $t'(pd\pi)$ etc. are now parameters and we take $t'(pd\pi) = 2$ eV/A, $t'(pp\sigma) = -2t'(pp\pi) = -3.5$ eV/A. We show in Fig. 1 the calculated temperature dependence of the yy -component of χ for $q=\Gamma L$ and ΓM . $\chi^{yy}(01, \Gamma L)$ and $\chi^{yy}(00, \Gamma L)$ are most sensitive to temperature and play an important role in the softening of the $L_1^{-}(1)$ mode.

Fig.1
Temperature variation of
 $\chi^{yy}(\mu\nu, q)$ for $q=\Gamma M, \Gamma L$.

3. Phonon dispersion curves.

The dynamical matrix is assumed to be the sum of the matrix $\chi^{\alpha\beta}(\mu\nu, q)$ obtained above and the matrix $R^{\alpha\beta}(\mu\nu, q)$ for short-range forces between ion-cores. In the calculation of the phonon dispersion curves, we do not use χ of the whole q values but introduce instead long-range forces between ions which reproduce the calculated χ at the symmetry points of $q=0, \Gamma A$, etc. cited above. These forces are found non-central and temperature-dependent. As for the matrix R we take five short-range potentials $\phi_{01}, \phi_{12}, \phi'_{12}, \phi_{00}$, and ϕ_{11} ⁵ and we specify these potentials by several parameters. We determined these parameters so as to get a good fit to the observed transverse phonon frequencies⁶ at the Γ, A, M, L points. The phonon dispersion curves calculated at 500 K are shown by solid curves in Fig. 2. The agreement with the observation is reasonably good. The dotted curves in Fig. 2 show the results for 0 K. As seen from the figure, all frequencies except those of the lowest dispersion curve along the ΓL line are insensitive to temperature. The $L_1^-(1)$ mode frequency becomes imaginary at 0 K. Thus, we conclude that the $L_1^-(1)$ mode freezes as lattice distortion at a certain temperature which is found to be 220 K.

Fig.2 The transverse phonon dispersion curves.

Dots denote experimental data obtained by Wakabayashi et al.⁶

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