PHYSICAL REVIEW B VOLUME 25, NUMBER 12 15 JUNE 1982

Theory of Raman scattering from charge-density-wave phonons

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(Received 2 November 1981; revised manuscript received 16 March 1982)

A recent microscopic theory of two-phonon Raman scattering by anomalous phonons in transition-metal compounds is extended to one-phonon scattering from phonons associated with a charge density wave (CDW). To lowest order in the CDW distortion the two-phonon results can be used directly. For layered transition-metal dichalcogenides the Raman intensities of the CDW modes result mainly from intralayer interactions. To understand observed intensities in $2H$-TaSe$_2$ anharmonicity and higher-order Raman coefficients are included within a Landau theory. For stronger distortions a general theory is possible, but a simple solution can only be given for a very simple model with a single conduction band and a single CDW wave vector. The simple solution for the Raman amplitude can be made analytic for the case of one dimension. Some conclusions are also drawn for more general cases.

I. INTRODUCTION

The layered dichalcongenides of the group-V b transition metals undergo phase transitions of the generalized charge-density-wave (CDW) type.[1] The CDW distorts the lattice statically by an amount roughly proportional to the onset temperature for this phase transition. The $2H$ polytypes of the compounds are typically found in normal phases at room temperature, except for the presence of anomalously soft LA-like phonons for wave vectors q near $2\Gamma M/3$ in the basal plane. Raman data on $2H$-TaSe$_2$ show that the strongest room-temperature peak is a two-phonon overtone of these modes.[2] The frequency of the peak decreases as the temperature is decreased,[3] in agreement with neutron data on the soft phonon.[4] Below the onset temperature $T_0 = 120$ K for the CDW the soft modes "condense" into CDW phonons, and a new low-frequency Raman peak appears and eventually evolves into two peaks of A symmetry and two peaks of E symmetry at very low temperatures.[3] If the lattice retains the same space group ($P6_3/mmc$) that it has in the normal phase,[5] then these modes and their symmetries ($2A_{1g}$ modes and $2E_{2g}$ modes) are just what is expected for vibrations of the commensurate $3a_0 \times 3a_0$ CDW superlattice studied by Moncton *et al.*[4] It has recently been shown that the commensurate phase of $2H$-TaSe$_2$ is orthorhombic, not hexagonal,[6] but no effect of this has yet been observed in the Raman spectra.

A similar strong two-phonon Raman spectrum is observed in the normal phase of $2H$-NbSe$_2$.[7,8] In this material the soft LA-like phonons condense at $T_0 = 33$ K to form an incommensurate CDW state with a superlattice that is approximately $3a_0 \times 3a_0$.[4] Below T_0 Raman-active CDW modes are seen,[7] one each of A and E symmetry.[9,10]

Interesting Raman results have also been obtained for the stronger CDW systems found in the $1T$ polytype, which are in distorted phases already above room temperature. $1T$-TaS$_2$ was studied by Smith *et al.*,[11] Duffey *et al.*,[12(a)] and by Sugai *et al.*[12(b)] the most complete study is that of Duffey *et al.* There are three distorted phases. The crystal forms in the incommensurate $1T_1$ phase. At 350 K the CDW wave vectors rotate into another incommensurate ($1T_2$) phase, which finally becomes commensurate at 190–200 K ($1T_3$ phase) with a $\sqrt{13}a_0 \times \sqrt{13}a_0 \times 13c_0$ superlattice containing 169 Ta atoms. The CDW Raman spectrum in the $1T_3$ phase is extremely rich.[12] Similar, but less spectacular, Raman spectra were observed in $1T$-TaSe$_2$.[11–13]

Hanamura and Nagaosa have discussed two microscopic mechanisms for the origin of the Raman scattering from CDW photons.[14] One mechanism involves a hybridization of the CDW phonon with Raman-active modes of the normal phase. This mechanism is often invoked in phenomenological theories of light scattering at phase transitions[15] wherein the order parameter couples to Raman-active degrees of freedom in the free energy. The second mechanism of Hanamura and Nagaosa involves scattering of photons from the electron-hole pair excitations that accompany the CDW phonons. I show here that this mechanism arises naturally from a previously discussed calculation of two-phonon Raman scattering by the anomalous phonons of the normal phase.[16] Such a mechanism is also often invoked in phenomenological theories,[15] which couple the polarizability fluctuation $\delta\alpha$ bilinearly to the phonon coordinates $u(q)$:

$$\delta\alpha=\sum_{q} M^{(2)}(\vec{q})u(\vec{q})u(-\vec{q}) \; . \tag{1}$$

After the soft phonons "condense" at T_0, u acquires a static component u_s and a dynamic component δu for selected wave vectors such as $\vec{q}_0$ and $-\vec{q}_0$:

$$u(\vec{q}_0)=u_s(\vec{q}_0)+\delta u(\vec{q}_0) \; . \tag{2}$$

The fluctuating polarizability will then contain contributions of the form

$$\delta\alpha=M^{(2)}(\vec{q}_0)[u_s(\vec{q}_0)\delta u(-\vec{q}_0) + u_s(-\vec{q}_0)\delta u(\vec{q}_0)] \; , \tag{3}$$

and the intensity of the resulting first-order (in δu) Raman scattering will be proportional to the square of u_s. Thus an approximate understanding of the Raman activity of the "new" CDW phonon modes can be simply based on our existing understanding of the strong two-phonon spectra in the normal phase.[16]

Section II contains a review of the CDW state and introduces the notation used to describe it. Section III describes the microscopic theory of Raman scattering in metals (in part A) and its application to the weak CDW case (in part B), which is essentially an explicit elaboration of Eq. (3). An application of the results will be made to 2*H*-TaSe$_2$, in Secs. III C and III D, where it will be shown that the observed strong Raman activity of phase modes results from intralayer anharmonicity and from higher-order terms in the Raman amplitude. These are discussed within a Landau theory, the details of which are given in the Appendix. Section III E develops the theory for a strong CDW in a simple case where results can be obtained analytically. Section III F completes the theory for one dimension. The discussion in Sec. III H draws some general conclusions for more realistic higher-dimensional strong CDW cases.

II. PRELIMINARIES

A. Mean-field theory

The microscopic mechanism for the Raman activity of CDW phonon modes is closely related to the electronic processes that within a harmonic mean-field theory (MFT) explain their "condensation." A convenient description is that of Kotani[17] which we generalize to three dimensions.

The Hamiltonian has the usual form in units where $\hbar=1$:

$$H=H_0+H' \; , \tag{4a}$$

where

$$H_0=H_e+H_p=\sum_{ka} E_{ak}c_{ak}^{\dagger}c_{ak} + \sum_{qj}\omega_{qj}^{0}b_{qj}^{\dagger}b_{qj} \tag{4b}$$

and

$$H'=\sum_{kdaqj}(d,k+q\,|\,V_j(-q)\,|\,ak) \times c_{d,k+q}^{\dagger}c_{ak}(b_{qj}+b_{-qj}^{\dagger}) \; . \tag{4c}$$

Here k is an electron wave vector, a and d are band indices, q is a phonon wave vector, j a phonon polarization index, and b_{qj} and c_{ak} are phonon and electron annihilation operators, respectively. We make the assumption that certain expectation values are nonzero, namely

$$\langle c_{d,k+q}^{\dagger}c_{ak}\rangle \; , \; \langle b_{qj}\rangle \; , \; \langle b_{-qj}^{\dagger}\rangle \tag{5}$$

for a few bands d,a close to the Fermi energy and for certain wave vectors $\vec{q}$. For layered compounds the "primary" values of $\vec{q}$ are $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$, three equivalent vectors in the basal plane that meet at angles of 120°. Harmonics are possible of the form

$$\vec{q}=n_1\vec{q}_1+n_2\vec{q}_2+n_3\vec{q}_3 \; , \tag{6}$$

where the n_j are integers. In the commensurate case only a finite number of $\vec{q}$'s satisfy Eq. (6) *modulo* a reciprocal-lattice vector; in the commensurate case the number is infinite. In MFT we keep H, as given by Eq. (4c), but interpret $c_{d,k+q}^{\dagger}c_{ak}$, b_{qj}, and $b_{-qj}^{\dagger}$ as fluctuations away from the expectation values in Eq. (5). The latter give to H additional electron and phonon terms δH_e and δH_p:

$$\delta H_e=\sum_{kda}\left[\sum_{qj}(d,k+q\mid V_j(-q)\mid ak)\langle b_{qj}+b^{\dagger}_{-qj}\rangle\right]c^{\dagger}_{d,k+q}c_{ak}\ , \tag{7a}$$

$$\delta H_p=\sum_{qj}\left[\sum_{kda}(d,k+q\mid V_j(-q)\mid ak)\langle c^{\dagger}_{d,k+q}c_{ak}\rangle\right](b_{qj}+b^{\dagger}_{-qj})\ . \tag{7b}$$

We find that

$$\langle b^{\dagger}_{-qj}\rangle=\langle b_{qj}\rangle=-\frac{1}{\omega^{0}_{qj}}\sum_{kda}(dk-q\mid V_j(q)\mid ak)\langle c^{\dagger}_{d,k-q}c_{ak}\rangle\ , \tag{8}$$

by requiring the vanishing of $\langle[b_{qj},(H_p+\delta H_p)]\rangle$ and $\langle[b^{\dagger}_{-qj},(H_p+\delta H_p)]\rangle$. Hence

$$\delta H_e=\sum_{kdaq}(d,k+q\mid V_s(-q)\mid ak)c^{\dagger}_{d,k+q}c_{ak}\ , \tag{9a}$$

where $V_s(-q)$ is the static potential of the CDW with matrix elements

$$(d,k+q\mid V_s(-q)\mid ak)=\sum_{j}(d,k+q\mid V_j(-q)\mid ak)\langle b_{qj}+b^{\dagger}_{-qj}\rangle\ . \tag{9b}$$

The presence of the mean-field potential $V_s(-q)$ makes the new electronic Green's function off-diagonal in k. This function is defined by

$$G_{ek;d,k+q}(i\omega_n)=-\tfrac{1}{2}\int_{-1/T}^{1/T}e^{i\omega_n\tau}\langle T_\tau[c_{k+qd}(\tau)c^{\dagger}_{ke}(0)]\rangle d\tau\ , \tag{10a}$$

where T_τ is the time-ordering operator for "time" τ, and $\omega_n=2\pi nT$, where T is the temperature in energy units and n is an integer. G obeys the equation

$$G_{ek;d,k+q}(i\omega_n)=\frac{1}{i\omega_n-E_{ek}+E_0}\left[\delta_{q0}\delta_{de}+\sum_{q'e'}G_{e',k+q';d,k+q}(i\omega_n)\langle k+q',e'\mid V_s(-q')\mid ke\rangle\right]\ , \tag{10b}$$

where δ_{q0} and δ_{de} are Kronecker deltas and E_0 is the chemical potential. The self-consistency condition follows by manipulating Eq. (10a):

$$\langle c^{\dagger}_{d',k'-q}c_{a'k'}\rangle=T\sum_{n}G_{d',k'-q;a'k'}(i\omega_n)\ . \tag{11}$$

To lowest order in V_s we have

$$G^{(0)}_{ek,ek}(i\omega_n)=\frac{1}{i\omega_n-E_{ek}+E_0}\ . \tag{12a}$$

We find to first order in V_s for $q\neq 0$

$$G^{(1)}_{ek;d,k+q}(i\omega_n)=\frac{(d,k+q\mid V_s(-q)\mid ek)}{(i\omega_n-E_{ek}+E_0)(i\omega_n-E_{d,k+q}+E_0)}\ . \tag{12b}$$

Using Eq. (12b), we perform the sum over n in Eq. (11), converting it to a contour integral in the usual way. The result is

$$\langle c^{\dagger}_{d',k'-q}c_{a',k'}\rangle_{(1)}=\frac{f_{d',k'-q}-f_{a',k'}}{E_{d',k'-q}-E_{a',k'}}(a'k'\mid V_s(-q)\mid d',k'-q)\ , \tag{13a}$$

where expressions of the form $f_{d,k}$ denote Fermi functions

$$f_{d,k}=(e^{(E_{dk}-E_0)/T}+1)^{-1}\ , \tag{13b}$$

where T is the temperature in energy units. When Eq. (13a) is substituted in Eq. (8), which is then substituted in Eq. (9b), we obtain a homogeneous linear equation for the matrix elements of $V_s(-q)$. A nonzero solution exists when

$$\det\left|\delta_{jj'}+\frac{2}{\omega_{qj}^{0}}\Pi_{jj'}(q,\omega=0)\right|=0\,, \tag{14}$$

where

$$\Pi_{jj'}(q,\omega)=\sum_{kcd}\frac{(ck\mid V_{j'}(-q)\mid d,k-q)(d,k-q\mid V_j(+q)\mid ck)(f_{d,k-q}-f_{ck})}{E_{d,k-q}-E_{ck}-\omega} \tag{15}$$

is the phonon self-energy.

Equation (14) determines the phase-transition temperature in mean-field theory. It is equivalent to the condition that in the high-temperature phase there exists a phonon of wave vector q and renormalized frequency equal to zero. It is expected that as the temperature is lowered Eq. (14) is satisfied first for a $\vec{q}$ equal to any of the primary wave vectors, $\vec{q}_i$ in Eq. (6).

B. Static distortion

From the general expression for the displacement $u_{\lambda\beta l}(n)$ in the βth Cartesian direction of the λth atom in the nth unit cell in layer l one finds

$$\langle u_{\lambda\beta l}(n)\rangle=\tfrac{1}{2}\sum_{q/2}[e_{\lambda\beta l}(\vec{q})e^{i\vec{q}\cdot\vec{R}_n}+e_{\lambda\beta l}(\vec{q})^{*}e^{-i\vec{q}\cdot\vec{R}_n}]\,, \tag{16a}$$

where

$$\tfrac{1}{2}e_{\lambda\beta l}(\vec{q})=\sum_{j}\frac{\epsilon^{\lambda\beta l}(qj)(\langle b_{qj}\rangle+\langle b^{\dagger}_{-qj}\rangle)}{\sqrt{2NM_{\lambda}\omega_{qj}^{0}}}\,. \tag{16b}$$

The sum in Eq. (16a) is over half of all the $\vec{q}$'s that contribute to the distortion such that the pair $(\vec{q},-\vec{q})$ occurs only once. The $\vec{q}$'s of interest lie in the basal plane, and we assume that $\vec{R}_n$ does also; its origin will be at a metal-atom site. In Eq. (16b) the $\epsilon^{\lambda\beta l}(qj)$ are components of the phonon eigenvector for mode (qj), M_λ is the mass of the atoms on sublattice λ, and N is the number of unit cells in the crystal.

For $1T$-type materials there is a single layer per unit cell in the undistorted phase. We drop the index l in Eqs. (16a) and (16b) and write

$$e_{\lambda\beta}(q)=\epsilon_{\lambda\beta}(q)e^{i\phi_{\lambda\beta}}\,, \tag{16c}$$

where the amplitudes $\epsilon_{\lambda\beta}(q)$ and phases $\phi_{\lambda\beta}$ are real. One may invert Eqs. (16b) and (16c) to obtain $\langle b_{qj}\rangle+\langle b^{\dagger}_{-qj}\rangle$ and then obtain the matrix elements of the static potential $V_s(-q)$:

$$(d,k+q\mid V_s(-q)\mid ak)=\tfrac{1}{2}\sqrt{N}\sum_{j}(d,k+q\mid V_j(-q)\mid ak)\sqrt{2\omega_{qj}^{0}}\sum_{\beta\lambda}\sqrt{M_\lambda}\,\epsilon_{\lambda\beta}(q)\epsilon^{\lambda\beta}(qj)^{*}e^{i\phi_{\lambda\beta}}\,. \tag{17a}$$

The CDW itself if often described by parameters that represent Fourier components of electronic charge density.[18–25] Ionic displacements are then essentially given by the gradient of the local charge density. This reduces the number of parameters in Eq. (17a) to those for an LA phonon. Thus Eq. (17a) may be approximated by

$$(d,k+q\mid V_s(-q)\mid ak)=\tfrac{1}{2}\sqrt{2N\omega_q^{0}M^{*}}\,(d,k+q\mid V_{\mathrm{LA}}(-q)\mid ak)\epsilon e^{i\phi} \tag{17b}$$

where ϵ and ϕ are close to $\epsilon_{\lambda\beta}$ and $\phi_{\lambda\beta}$ for λ and β corresponding to displacements of the metal atom along q. M^{*} is an effective mass that is not too different from the metal-atom mass.

The undistorted structure of $2H$-TaSe$_2$ has two TaSe$_2$ layers per unit cell with a center of inversion halfway between the two Ta atoms. Lattice vectors $\vec{R}_n$ in the basal plane will locate these centers of inversion. The layers will be labeled by $l=1,2$. The inversion operation takes site λ in layer 1 into site λ in layer 2. Equation (16c) now becomes

$$e_{\lambda\beta l}(q)=\epsilon_{\lambda\beta}(q)\exp\{i[(-1)^{l}\phi_{\lambda\beta l}(q)+\phi_0]\}\,. \tag{18}$$

Inversion symmetry is maintained in the distorted phase if $\phi_0=\pm\pi/2$ and if

$$\phi_{\lambda\beta 1}(q)=\phi_{\lambda\beta 2}(q)+2\vec{q}\cdot\vec{d},\ \ \mathrm{mod}(2\pi)\,, \tag{19a}$$

where the inversion center is now at $\vec{R}_n=\vec{d}$. Now introduce three nearest-neighbor lattice vectors in the basal plane, $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, making angles of 120° with one another, and making 30° angles with $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$, respectively, so that

$$\vec{q}_i\cdot\vec{a}_{i+1}=0\ ,\quad \vec{a}_i\cdot\vec{q}_i=2\pi/3\ . \tag{19b}$$

Then if $\vec{d}$ is written

$$\vec{d}=\sum_i m_i\vec{a}_i\ , \tag{19c}$$

where $m_i=0,1,2$, we find for Eq. (19a)

$$\phi_{\lambda\beta 1}(q_1)=\phi_{\lambda\beta 2}(q_1)+4\pi(m_1-m_3)/3\ ,\quad \mathrm{mod}(2\pi)+\mathrm{c.p.} \tag{19d}$$

In the spirit of Eq. (17b) we now consider a phonon "basis" consisting of LA modes in each layer. These will be assumed to be degenerate with frequency ω_q^0. This gives

$$(d,k+q\,|\,V_s(-q)\,|\,ak)=\tfrac{1}{2}\sqrt{2N\omega_q^0M^*}\,\epsilon e^{i\phi_0}\sum_l (d,k+q\,|\,V_l(-q)\,|\,ak)\exp[i(-1)^l\phi_{ql}]\ , \tag{20}$$

where $V_l(-q)$ is the electron-phonon perturbation for an LA mode in layer l.

We keep a q dependence and an l dependence to the phases ϕ_{ql} in Eq. (20), as allowed by the most general Landau theory allowed by symmetry, namely that of Jacobs and Walker.[24] Recent electron-diffraction experiments performed on a cold stage in an electron microscope by Fung *et al.*[6] show that the low-temperature commensurate CDW state of $2H$-TaSe$_2$ is orthorhombic rather than hexagonal, as thought previously. The space group is either $Cmc2_1$ or $Cmcm$, which is favored and which has a center of inversion. Recent theoretical work[26–28] has shown that $Cmcm$ structures can be obtained for certain values of the Landau parameters. Such theories can also explain the existence of the "striped" phase first seen in the x-ray diffraction studies of Fleming *et al.*[29] and then in electron microscope images by Chen *et al.*[30] and by Fung *et al.*[6] This phase has one commensurate and two incommensurate wave vectors. These theories also seem able to explain the reentrant nature of the pressure dependence of the commensurate states discovered by McWhan *et al.*[31]

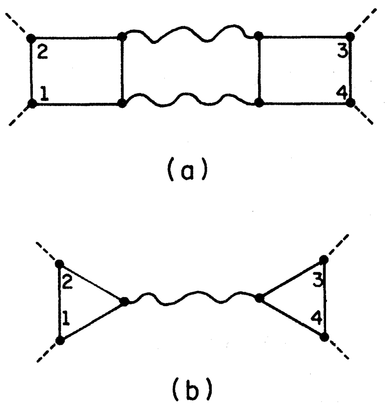

FIG. 1. Four-vertex functions for Raman scattering. Straight lines represent electron Green's functions. Wiggly lines represent phonon Green's functions. At vertices 1 and 4 are matrix elements of the operator p_i and at vertices 2 and 3 are matrix elements of the operator p_s, where p_i and p_s are projections of the momentum along polarization directions for incident and scattered photons, respectively.

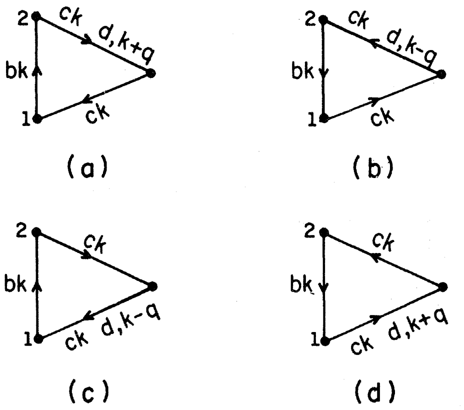

FIG. 2. Four different contributions to the left-hand electron loop of Fig. 1(b) for a CDW phonon. At the right-hand vertex is a matrix element of $V_{j'}(q)$. The vertical line (bk) represents a Green's function for an excited state assumed to be unaffected by the CDW. The line labeled ck represents the diagonal electron Green's function $G_{ck,ck}$. Those with two labels represent nondiagonal Green's function, e.g., $ck\rightarrow d,k+q$ denotes the Green's function $G_{ck;d,k+q}$.

III. RAMAN SCATTERING CALCULATION

A. General

It is convenient to use a Green's-function method that describes Raman scattering as essentially the imaginary part of an irreducible four-vertex function.[32] Diagrams similar to Fig. 1(a) were previously used to describe two-phonon Raman scattering.[16] One-phonon scattering is described by Fig. 1(b).[33] In the case of interest here, the electron lines and electron-phonon and electron-photon matrix elements are those of the distorted CDW state. Some progress has been made in calculating the relevant parameters,[34] and a direct calculation of the electron loops in Fig. 1(b) may be possible.

We choose another approach that is formally equivalent to a direct calculation but allows for a perturbation expansion in the static CDW potential V_s. Our approach uses normal-state electron and phonon basis functions. This means that the matrix elements at the electron-photon and electron-phonon vertices are those of the undistorted state. The Green's functions are no longer diagonal in wave vector. The electron Green's functions obey Eqs. (10a) and (10b).

The electron-phonon interaction, H' of Eq. (4c), mixes wave vectors $\pm q$ in the phonon Green's function,[35]

$$\begin{aligned} D_{qj,q'j'}(i\omega_n) &= \langle\langle (b_{q'j'}+b^{\dagger}_{-q'j'});(b^{\dagger}_{qj}+b_{-qj})\rangle\rangle \\ &\equiv -\int_0^{1/T} e^{i\omega_n\tau}\langle T_\tau[b_{q'j'}(\tau)+b_{-q'j'}(\tau)^{\dagger}][b_{qj}(0)^{\dagger}+b_{-qj}(0)]\rangle d\tau\ . \end{aligned} \tag{21}$$

For $\vec{q}$ equal to one of the primary $\vec{q}_j$, examination of the Dyson equation[35] for D reveals that its off-diagonal elements are strong only when $\vec{q}\,'=\pm\vec{q}$ in Eq. (21).

The important contributions to the four-vertex function in Fig. 1(b) take the form

$$\mathscr{F} = -\sum_{\substack{qq'\\jj'}} L_{qj'}D_{qj',q'j}L'_{q'j'}\ , \tag{22a}$$

where

$$L_{qj'} = L^{(a)}_{qj'} + L^{(b)}_{qj'} + L^{(c)}_{qj'} + L^{(d)}_{qj'}\ , \tag{22b}$$

and where $L^{(a)}_{qj'}$, $L^{(b)}_{qj'}$, $L^{(c)}_{qj'}$, and $L^{(d)}_{qj'}$ are represented by the diagrams in Figs. 2(a), 2(b), 2(c) and 2(d), respectively. A similar decomposition holds for $L'_{qj'}$.

We assume that band b couples neither to the phonons nor to V_s; this is consistent with the assumption made earlier for two-phonon Raman scattering.[16] A similar assumption was made by Hanamura and Nagaosa.[14] The Matsubara frequencies $i\omega_\mu$ and $-i\omega_\mu+i\omega_t$ are to be added to the electron loop at the vertices 1 and 2, where $\omega_\mu=2\pi T\mu$, $\omega_t=2\pi Tt$, and where μ and t are integers. Introducing $\omega_n=2\pi Tn$, where n is an integer, we find

$$\begin{aligned} L_{qj'} = T\sum_n\sum_{kbcd} &\left[\frac{(ck\,|\,p_s\,|\,bk)(bk\,|\,p_i\,|\,ck)}{(i\omega_n+i\omega_\mu-E_{bk}+E_0)} + \frac{(ck\,|\,p_i\,|\,bk)(bk\,|\,p_s\,|\,ck)}{(i\omega_n+i\omega_t-i\omega_\mu-E_{bk}+E_0)}\right] \\ &\times[G_{ck;d,k+q}(i\omega_n+i\omega_t)(ck\,|\,V_{j'}(q)\,|\,d,k+q)G_{ck,ck}(i\omega_n) \\ &+G_{ck,ck}(i\omega_n+i\omega_t)(d,k-q\,|\,V_{j'}(q)\,|\,ck)G_{d,k-q;ck}(i\omega_n)]\ , \end{aligned} \tag{23}$$

where $p_i=\vec{p}\cdot\vec{e}_i$ and $p_s=\vec{p}\cdot\vec{e}_s$, where E_0 is the chemical potential, and where $E_{bk}+E_0$ is the energy of band b, wave vector k.

B. Weak CDW

For a weak V_s, we may use Eqs. (12a) and (12b) in Eq. (23). The result is the same as that for two-phonon Raman scattering,[16] where the diagrams are those of Fig. 5 of Ref. 16 with two changes: at vertex

j, where there was a matrix element of $V_j(-q)$, there is now a matrix element of $V_s(-q)$, and in the energy denominators the phonon frequency $\omega_{j,-q}$ is replaced by zero.

We may therefore use the results of Ref. 16 in evaluating the sum over n in Eq. (23). We make the approximation that terms with double photon resonances dominate, which leads to Eq. (37) of Ref. 16 for two-phonon scattering. We also make the adiabatic, or frozen phonon, approximation. We also neglect spin effects and use time reversal arguments[16] to obtain [dropping explicit reference to the wave vector k, and using $d+$ to denote $(d,k+q)$]

$$L_{qj}=-\sum_{kcd}P_{is}(ck)(c\,|\,V_j(q)\,|\,d+)(d+\,|\,V_s(-q)\,|\,c)\frac{f_{d+}-f_c}{E_{d+}-E_c}\ . \tag{24a}$$

Here

$$\begin{aligned}P_{is}(ck)=\sum_{b\neq c}&[(c\,|p_s\,|\,b)(b\,|p_i\,|\,c)+(c\,|p_i\,|\,b)(b\,|p_s\,|\,c)]\\&\times[(E_b-E_c-\omega_l-i\gamma_b)^{-2}+(E_b-E_c+\omega_l+i\gamma_b)^{-2}]\ ,\end{aligned} \tag{24b}$$

with ω_l equal to the average of incident and scattered photon frequencies. We may also write

$$L_{-qj}=\sum_{kcd}P_{is}(ck)(c\,|\,V_s(q)\,|\,d+)(d+\,|\,V_j(-q)\,|\,c)\,\frac{f_{d+}-f_c}{E_{d+}-E_c}\ . \tag{24c}$$

For $1T$-type samples where Eq. (17b) holds for a single conduction band (c), we have

$$L_{qj}=\tfrac{1}{2}\sqrt{N}e^{i\phi}(\epsilon/u_0)N_{is}(q,\text{LA})\ , \tag{25a}$$

where

$$u_0=(2\omega_q^0M^*)^{-1/2} \tag{25b}$$

is a root-mean-square amplitude for the LA mode, and where N_{is} obeys

$$N_{is}(q,\text{LA})=-\sum_{k}P_{is}(ck)\,|\,(c\,|\,V_{\text{LA}}(q)\,|\,c+)\,|^2\frac{f_{c+}-f_c}{E_{c+}-E_c}\ . \tag{25c}$$

We also have

$$L_{-qj}=\tfrac{1}{2}\sqrt{N}e^{-i\phi}(\epsilon/u_0)N_{is}(q,\text{LA})\ . \tag{25d}$$

Note that if $P_{is}(ck)$ can be treated as a constant, $N_{is}(q,\text{LA})$ is proportional to the phonon self-energy $\Pi_{\text{LA,LA}}(q,\omega=0)$ of Eq. (15). This idea is developed more fully in Ref. 16. Here the self-energy Π is that of a metastable normal state at temperature $T<T_0$. Note also that $N_{is}(q,\text{LA})/\sqrt{2}$ equals $M_{is}^{(2)}(-q,\text{LA},0;q,\text{LA},0)$, the matrix element for the two-LA-phonon overtone scattering in Eq. (37) of Ref. 16.

For each primary q we make a unitary transformation to b_η^q and b_ϕ^q, with phonon annihilation operators representing amplitude and phase fluctuations:

$$\sqrt{2}b_\eta^q=b_qe^{-i\phi}+b_{-q}e^{i\phi}\ , \tag{26a}$$

$$i\sqrt{2}b_\phi^q=b_qe^{-i\phi}-b_{-q}e^{i\phi}\ . \tag{26b}$$

The Raman intensity is then proportional to the imaginary part as $i\omega_t\rightarrow\omega_0+i\epsilon$ of

$$\mathscr{F}(i\omega_t)=-N(\epsilon/u_0)^2\sum_{qq'}N_{is}(q,\text{LA})N_{is}(q',\text{LA})^*D_{\eta\eta}^{qq'}(i\omega_t)\ , \tag{27}$$

where

$$\begin{aligned}D_{\eta\eta}^{qq'}(i\omega_t)&=\langle\!\langle[b_\eta^{q'}+(b_\eta^{q'})^\dagger];[(b_\eta^q)^\dagger+b_\eta^q]\rangle\!\rangle\\&\equiv-\int_0^{1/T}e^{i\omega_t\tau}\langle T_\tau[b_\eta^{q'}(\tau)+b_\eta^{q'}(\tau)^\dagger][b_\eta^q(0)^\dagger+b_\eta^q(0)]\rangle d\tau\ .\end{aligned} \tag{28}$$

Anharmonic coupling will mix the b_η^q (and b_ϕ^q) for the three different primary q's and produce amplitude and phase modes of A_{1g} and E_g symmetry. Introducing the annihilation operators b_η^A for the A_{1g} mode and b_η^{E1} and b_η^{E2} for the doubly degenerate E_g mode, we find that the transformations are

$$b_\eta^{q3}=\frac{1}{\sqrt{3}}b_\eta^A+\frac{2}{\sqrt{6}}b_\eta^{E2}\ , \tag{29a}$$

$$b_\eta^{q1}=\frac{1}{\sqrt{3}}b_\eta^A+\frac{1}{\sqrt{2}}b_\eta^{E1}-\frac{1}{\sqrt{6}}b_\eta^{E2}\ , \tag{29b}$$

$$b_\eta^{q2}=\frac{1}{\sqrt{3}}b_\eta^A-\frac{1}{\sqrt{2}}b_\eta^{E1}-\frac{1}{\sqrt{6}}b_\eta^{E2}\ . \tag{29c}$$

Then Eq. (27) becomes

$$\mathscr{F}(i\omega_t)=-N(\epsilon/u_0)^2\left[\tfrac{1}{6}\left|{\sum}' N_{is}(q)\right|^2 D_{\eta\eta}^{AA}+\tfrac{1}{12}D_{\eta\eta}^{E2E2}\,|2N_{is}(q_3)-N_{is}(q_1)-N_{is}(q_2)|^2 \right.$$
$$\left. +\tfrac{1}{4}D_{\eta\eta}^{E1E1}\,|N_{is}(q_1)-N_{is}(q_2)|^2\right] \tag{30a}$$

Since the E modes are degenerate, their Green's functions equal a common $D_{\eta\eta}^{EE}$. Equation (30a) can then be written after use of symmetry arguments,

$$\mathscr{F}(i\omega_t)=-\tfrac{3}{8}N(\epsilon/u_0)^2\{[\,|N_{xx}(q_1)+N_{yy}(q_1)|^2D_{\eta\eta}^{AA}+|N_{xx}(q_1)-N_{yy}(q_1)|^2D^{EE}](\vec{e}_i\cdot\vec{e}_s)^2$$
$$+|N_{xx}(q_1)-N_{yy}(q_1)|^2D_{\eta\eta}^{EE}\,|\vec{e}_i\times\vec{e}_s|^2\}\ , \tag{30b}$$

where $\vec{e}_i$ and $\vec{e}_s$ are photon polarization vectors lying in the basal plane, and where $N_{xx}(q_1)$ and $N_{yy}(q_1)$ are calculated with the x axis parallel to the primary $\vec{q}$ vector $\vec{q}_1$.

Inversion symmetry holds in each layer of the $1T$ polytypes. Since amplitude and phase modes have opposite parity, the amplitude-mode Green's functions $D_{\eta\eta}^{AA}$ and $D_{\eta\eta}^{EE}$ appearing in Eq. (30b) will show no mixing from phase modes, even with anharmonicity present. If damping is neglected, the imaginary parts of $D_{\eta\eta}^{AA}$ and $D_{\eta\eta}^{EE}$ for $i\omega_t\rightarrow\omega_0+i\epsilon$ will give $2\omega_{q\mathrm{LA}}\delta(\omega_0-\omega_\eta^A)$ and $2\omega_{q\mathrm{LA}}\delta(\omega_0-\omega_\eta^E)$, respectively.

For $2H$ polytypes we use Eq. (20) in Eqs. (24a) and (24c) to obtain

$$L_{\pm q_1}=\tfrac{1}{2}\sqrt{N}(\epsilon/u_0)e^{\pm i\phi_0}[e^{\mp i\phi_{q_1}}N_{is}(q,11)+e^{\pm i\phi_{q_2}}N_{is}(q,12)]\ , \tag{31a}$$

$$L_{\pm q_2}=\tfrac{1}{2}\sqrt{N}(\epsilon/u_0)e^{\pm i\phi_0}[e^{\mp i\phi_{q_1}}N_{is}(q,21)+e^{\pm i\phi_{q_2}}N_{is}(q,22)]\ , \tag{31b}$$

where

$$N_{is}(q,ll')=-\sum_{kcd}P_{is}(ck)(c\,|\,V_l(q)\,|\,d+)(d+\,|\,V_{l'}(-q)\,|\,c)\left[\frac{f_{d+}-f_c}{E_{d+}-E_c}\right]. \tag{31c}$$

The inversion symmetry of the $2H$ structure may be used to show that

$$N_{is}(q,11)=N_{is}(q,22) \tag{31d}$$

and

$$N_{is}(q,12)=N_{is}(q,21)\ . \tag{31e}$$

Equation (22a) says that the four-vertex function may be written in the form

$$\mathscr{F}=-\langle\langle Q;Q\rangle\rangle\ , \tag{32a}$$

where

$$Q={\sum_{ql}}'[L_{ql}(b_{ql}^\dagger+b_{-ql})+L_{-ql}(b_{-ql}^\dagger+b_{ql})]\ . \tag{32b}$$

We introduce operators for amplitude ($b_{\eta l}^q$) and phase modes ($b_{\phi l}^q$) for each layer by the transformations:

$$e^{-i(\phi_0-\phi_{q_1})}b_{q_1}=\tfrac{1}{2}(b^q_{\eta 1}-ib^q_{\phi 1})\ , \tag{33a}$$

$$e^{-i(\phi_0+\phi_{q_2})}b_{q_2}=\tfrac{1}{2}(b^q_{\eta 2}+ib^q_{\phi 2})\ , \tag{33b}$$

$$e^{i(\phi_0-\phi_{q_1})}b_{-q_1}=\tfrac{1}{2}(b^q_{\eta 1}+ib^q_{\phi 1})\ , \tag{33c}$$

$$e^{i(\phi_0+\phi_{q_2})}b_{-q_2}=\tfrac{1}{2}(b^q_{\eta 2}-ib^q_{\phi 2})\ . \tag{33d}$$

This gives

$$Q=\left[\frac{N}{2}\right]^{1/2}\frac{\epsilon}{u_0}\sum_q{}'\{N_{is}(q,11)(b^q_{\eta 1}+b^{q\dagger}_{\eta 1}+b^q_{\eta 2}+b^{q\dagger}_{\eta 2})+N_{is}(q,12)[(b^q_{\eta 1}+b^{q\dagger}_{\eta 1}+b^q_{\eta 2}+b^{q\dagger}_{\eta 2})\cos(\phi_{q1}+\phi_{q2}) \\ -(b^q_{\phi 1}+b^{q\dagger}_{\phi 1}+b^q_{\phi 2}+b^{q\dagger}_{\phi 2})\sin(\phi_{q1}+\phi_{q2})]\}\ . \tag{34}$$

Interlayer electronic couplings, which produce a non zero value for $N_{is}(q,12)$, are seen from Eq. (34) to make the phase mode operators $b^q_{\phi 1}$ and $b^q_{\phi q}$ Raman-active. We can estimate the magnitude of $|N_{is}(q,11)|$ by comparing Eq. (31c) with Eq. (15). Thus

$$\left|\frac{N_{is}(q,12)}{N_{is}(q,11)}\right|\sim\left|\frac{\Pi_{12}(q,\omega=0)}{\Pi_{11}(q,\omega=0)}\right|\approx\frac{1}{2}\frac{(\Delta\omega^2)_{\mathrm{IL}}}{(\Delta\omega^2)_r}\ . \tag{35a}$$

In Eq. (35a) Π_{12} is the interlayer term in the phonon self-energy owing to the d electrons, and Π_{11} is the intralayer term in the self-energy. We estimate $|\Pi_{12}|$ by assuming that it is solely responsible for the observed interlayer phonon splitting $(\Delta\omega^2)_{\mathrm{IL}}$ of $(24\ \mathrm{cm}^{-1})^2$,[5] and we estimate $|\Pi_{11}|$ to be $(\Delta\omega^2)_r\sim(96\ \mathrm{cm}^{-1})^2$ from the size of the anomaly in the room-temperature dispersion curve.[4] Thus we estimate

$$\left|\frac{N_{is}(q,12)}{N_{is}(q,11)}\right|\sim 0.03\ , \tag{35b}$$

and find that the intrinsic Raman activity of the phase modes, as represented by the $\sin(\phi_{q1}+\phi_{q2})$ terms in Eq. (34) would give an intensity 0.1% or less of that from the amplitude modes. Thus it is probably correct to approximately Q in Eq. (34) by

$$Q=\left[\frac{N}{2}\right]^{1/2}\frac{\epsilon}{u_0}\sum_q{}'N_{is}(q)(b^q_{\eta 1}+b^{q\dagger}_{\eta 1}+b^q_{\eta 2}+b^{q\dagger}_{\eta 2})\ , \tag{36a}$$

where

$$N_{is}(q)=N_{is}(q,11)\ , \tag{36b}$$

as given by Eq. (31c) for a single layer. Transformations like Eqs. (29a) and (29c) may then be made to A and E amplitude-mode coordinates for each layer. Equation (36a) then becomes

$$Q=\left[\frac{N}{2}\right]^{1/2}\frac{\epsilon}{u_0}\left[\frac{1}{\sqrt{3}}[N_{is}(q_1)+N_{is}(q_2)+N_{is}(q_3)](b^A_{\eta 1}+b^{A\dagger}_{\eta 1}+b^A_{\eta 2}+b^{A\dagger}_{\eta 2}) \\ +\frac{1}{\sqrt{6}}[2N_{is}(q_3)-N_{is}(q_1)-N_{is}(q_2)](b^{E2}_{\eta 1}+b^{E2\dagger}_{\eta 1}+b^{E2}_{\eta 2}+b^{E2\dagger}_{\eta 2}) \\ +\frac{1}{\sqrt{2}}[N_{is}(q_1)-N_{is}(q_2)](b^{E1}_{\eta 1}+b^{E1\dagger}_{\eta 1}+b^{E1}_{\eta 2}+b^{E1\dagger}_{\eta 2})\right]\ . \tag{37}$$

C. Stronger CDW effects: Anharmonicity

How then do we explain the experimental observation of four strong CDW phonon modes ($2A$ plus $2E$) at low temperatures in $2H$-TaSe$_2$?[3,5] Third- and higher-order anharmonic couplings act within each layer to split each triply degenerate set of modes into A and E amplitude modes and A and E phase modes. Each layer lacks inversion symmetry. These perturbations will also couple E amplitude modes with E phase modes. In the Appendix it is shown using the Landau theory of Jacobs and Walker[24] that the terms that couple E amplitude and E phase modes are comparable with those that give the splitting between amplitude and phase modes. No such coupling occurs for A modes. Furthermore, the ratio of coupling to splitting [$\tan\delta$ in Eq. (A10)] remains finite as the CDW amplitude ϵ tends to zero. Since this mixing of modes of opposite parity is large, the new coupled modes will both be rather strongly Raman-active but the stronger modes will be those with the greater amplitude-mode character, which we denote "amplitudelike."

Introducing annihilation operators $B^{\gamma}_{\eta l}$ and $B^{\gamma}_{\phi l}$ for amplitudelike and phaselike modes of symmetry $\gamma = E_1, E_2$ in layer l, we can write the transformation in the form

$$b^{\gamma}_{\eta l} = \cos\theta_{\gamma} B^{\gamma}_{\eta l} - \sin\theta_{\gamma} B^{\gamma}_{\phi l} \ , \tag{38a}$$

$$b^{\gamma}_{\phi l} = \sin\theta_{\gamma} B^{\gamma}_{\eta l} + \cos\theta_{\gamma} B^{\gamma}_{\eta l} \ , \tag{38b}$$

where $\theta_{E1} = \theta_{E2} = \delta/2$. This is the reverse transformation to that in Eqs. (A11c) and (A11d). Thus far the degeneracy of $E1$ and $E2$ is maintained.

We now consider the effects of the weak interlayer coupling. Its static effect is extremely important. As recent theoretical work has shown,[26–28] it causes the reentrant lock-in transition under pressure,[31] and its competition with intralayer terms causes the stripes and textures in the incommensurate states.[29,30,6] A dynamical effect of interlayer coupling is the splitting of the degeneracy of CDW modes in layers 1 and 2.[5,25] If the low-temperature phase has inversion symmetry, the number of Raman-active modes does not change, but for $\gamma = A$, $E1$, and $E2$ there is a splitting into Raman-active symmetric (s) and infrared-active antisymmetric (a) states whose annihilation operators obey

$$B^{\gamma}_{\eta s,a} = \frac{1}{\sqrt{2}}(B^{\gamma}_{\eta 1} \pm B^{\gamma}_{\eta 2}) \ , \tag{38c}$$

$$B_{\phi s,a} = \frac{1}{\sqrt{2}}(B^{\gamma}_{\phi 1} \pm B^{\gamma}_{\phi 2}) \ . \tag{38d}$$

If the inversion center is at $\vec{d} = 0$ [see Eqs. (19a), (19c) and (19d)] the resulting symmetry is that of the high-temperature phase, $P6_3(D_{6h})$, but if $\vec{d} \neq 0$, the structure is orthorhombic (D_{2h}). Suppose $\vec{d}$ is perpendicular to $\vec{q}_3$. Then the $E2$ modes of a single layer become A_g plus A_u of D_{2h}, the $E1$ modes become B_{1g} plus B_{1u}, and the A modes (actually A_1 modes) become A_g plus A_u.

In the D_{2h} case the interlayer coupling will cause θ_{E1} to differ slightly from θ_{E2} in Eqs. (38a) and (38b). This coupling will also cause weak mixing of $B^{E2}_{\eta s}$ with $B^{A}_{\eta s}$ and of $B^{E2}_{\phi s}$ with $B^{A}_{\phi s}$. If the latter mixing is neglected, the intensity of the Raman scattering from the E modes can be obtained from the square modulus of the coefficients of $B^{\gamma}_{\eta s}$ and $B^{\gamma}_{\phi s}$ after Eqs. (38a)–(38d) are substituted in Eq. (37). The orthorhombic phase shows multiple twinning of a scale of 1 μm or less.[6] The resulting expression should therefore be averaged over all permutations of $\vec{q}_1$, $\vec{q}_2$, and $\vec{q}_3$ for fixed photon polarization vectors $\vec{e}_i$ and $\vec{e}_s$. When this is done, we recover Eq. (30b) with $D^{EE}_{\eta\eta}$ replaced by

$$(\cos^2\theta_{E1} D^{E1E1}_{\eta s \eta s} + \sin^2\theta_{E1} D^{E1E1}_{\phi s \phi s} + \cos^2\theta_{E2} D^{E2E2}_{\eta s \eta s} + \sin^2\theta_{E2} D^{E2E2}_{\phi s \phi s}) \ . \tag{39}$$

D. Higher-order Raman coefficients

The above treatment of Raman scattering from a weak CDW is inconsistent in the following sense. Whereas we essentially expanded the Raman amplitude to second order in CDW phonon coordinates and took terms bilinear in static and dynamic displacements, it was necessary to consider third- and fourth-order terms in the free energy in order to discuss properly the CDW lattice dynamics. If third- and fourth-order terms are important for the free energy, they should also be important for the Raman amplitude. Just as the factor that multiplies P_{is} in Eqs. (25c) or (31c) integrates to give the phonon self-energy [Eq. (15)], so that the Raman amplitude scales with the self-energy, so do the third- or higher-order terms in the integral for the Raman amplitude that have two-photon energy denominators scale with the respective higher-order electron-mediated, higher-order anharmonic-coupling coefficients. This was shown explicitly in Ref. 16 for the third-order case. Thus to each term in the Landau expansion of the free energy there should correspond a term in the amplitude for scattering of a photon polarized along the i direction in the basal plane into a photon polarized along the s direction in the plane. The second-order intralayer coefficient $A+B\delta^2$ of the Landau expansion of the free energy Eq. (A1b) corresponds to

$$N_{is}(q,11)=N_{is}(q,22)$$

of Eq. (31c), and the interlayer coeffiicent L of Eq. (A1c) corresponds to $N_{is}(q,12)$. To the term $G\,|\,\psi_{lj}\,|^4$ in the free energy there should be a Raman amplitude $G_{is}(j)\,|\,\psi_{lj}\,|^4$, where the tensor $G_{is}(j)$ has principal axis along $\vec{q}_j$. $K\,|\,\psi_{lj}\psi_{lj+1}\,|^2$ should correspond to

$$K_{is}(j+2)\,|\,\psi_{lj}\psi_{lj+1}\,|^2\ ,$$

where the tensor $K_{is}(j+2)$ has a principal axis along $\vec{q}_{j+2}$. In each case we expand to first order in the $\delta\psi_{lj}$. The D term produces only an isotropic tensor and will lead to a Raman amplitude for layer 1 of the form $Q_D\delta_{is}$, where

$$Q_D=-\,|\,D'\,|\,\epsilon^2[\cos(\phi'_D+2\pi m/3+3\theta)\sqrt{3}\alpha_A \\ -\sin(\phi'_D+2\pi m/3+3\theta)\sqrt{3}\beta_A]\ , \tag{40}$$

where

$$\alpha_A=\frac{u_0}{\epsilon\sqrt{N}}(b^{A}_{\eta 1}+b^{A\dagger}_{\eta 1})\ , \tag{41a}$$

and

$$\beta_A=\frac{u_0}{\epsilon\sqrt{N}}(b^{A}_{\phi 1}+b^{A\dagger}_{\phi 1})\ . \tag{41b}$$

We expect an approximate proportionality between $|\,D'\,|\,e^{-i\phi_{D'}}$ and $|\,D\,|\,e^{-i\phi_D}$ of Eq. (A3a). Similar expressions may be written for the isotropic parts of the Raman amplitude associated with the G, K, E, and M terms of the free energy; the lowest-order contribution is from D-like and E-like terms and is proportional to ϵ^2. Such terms are necessary to explain the nonzero intensity of the A phase mode. They will also make an important additional contribution to the Raman amplitude from the A amplitude mode, and their anisotropic counterparts will make important additional contributions to the Raman amplitude from the E amplitude and phase modes. Such expressions can be explicitly worked out, but they will have far too many parameters to be useful in data analysis.

The above considerations about intensity of the coupled amplitude and phase modes suggest that the data of Refs. 3 and 5 on $2H$-TaSe$_2$ at low temperature be interpreted as follows: The 80-cm^{-1} A peak and the 50-cm^{-1} E peak correspond to amplitudelike modes, and the 40-cm^{-1} A peak and the 63-cm^{-1} E peaks correspond to the phaselike modes. The recent data of Sugai *et al.*[12(b),36] support this assignment, which is different from the original one made by Holy *et al.*[5]; they assigned the higher-frequency mode of each symmetry to the amplitude mode. Sooryakumar *et al.*[9] and Sugai *et al.*[12(b),36] studied the evolution of the CDW Raman modes as the temperature is raised. There is considerable broadening and some softening. The A modes seem to merge together, and perhaps the E modes also, as the transition temperature to the striped phase is approached from below. There is a suggestion that the A phase mode loses intensity more rapidly with rising temperature than do the other modes[12(b),36] but more precise data are needed to reach a firm conclusion. (See note added in proof.)

E. Strong CDW

The electronic Green's function G that appears in Eq. (23) cannot be approximated by Eqs. (12a), and (12b) for a strong static perturbation $V_s(q)$. A solution for $G_{k,k+q}$ can be obtained for a single electronic band coupled to a single primary q. Then $\vec{k}$ will couple only to $\vec{k}+\vec{q}$ if $\vec{k}$ is in the "left" half of the Brillouin zone near $-\vec{q}/2$. The approximation is exact if $2\vec{q}$ is a reciprocal-lattice vector.[17]

For simplicity we let

$$V_q=(k+q\,|\,V_{\mathrm{LA}}(-q)\,|\,k) \tag{42a}$$

be real and independent of k, and set the phase ϕ_0 of the CDW equal to zero. Then by Eqs. (17b) and (25b) we have

$$\sqrt{N}(\epsilon/u_0)V_q\equiv\Delta\ . \tag{42b}$$

Equation (10b) has the solutions

$$G_{kk}(i\omega_n)=\frac{i\omega_n-E_{k+q}}{\mathscr{D}(i\omega_n)}\ , \tag{43a}$$

$$G_{k+q,k+q}(i\omega_n)=\frac{i\omega_n-E_k}{\mathscr{D}(i\omega_n)}\ , \tag{43b}$$

$$G_{k,k+q}(i\omega_n)=G_{k+q,k}(i\omega_n)=\Delta/\mathscr{D}(i\omega_n)\ , \tag{43c}$$

where

$$\mathscr{D}(i\omega_n)=(i\omega_n-E_k)(i\omega_n-E_{k+q})-\Delta^2\ . \tag{43d}$$

This can also be written

$$\mathscr{D}(i\omega_n)=(i\omega_n-E_1)(i\omega_n-E_2)\,, \tag{44a}$$

where

$$E_{1,2}=E_{1,2}(k,k+q)$$
$$=\frac{E_k+E_{k+q}}{2}\pm\left[\left[\frac{E_k-E_{k+q}}{2}\right]^2+\Delta^2\right]^{1/2} \tag{44b}$$

are the energies of the new coupled electronic states. Note that E_1 is greater than E_2 by at least the CDW "gap" 2Δ.

We evaluate the energy E_{bk} and the momentum matrix elements in Eq. (23) for $k=\pm q/2$. We assume that these matrix elements are real. We rewrite the second term in the second factor of Eq. (23) by making the replacement of $\vec{k}+\vec{q}$ for $\vec{k}$. This gives (dropping the phonon polarization index j but keeping the band index b of the excited electronic state)

$$L_q^{(a)}+L_q^{(c)}=L_{-q}^{(a)}+L_{-q}^{(c)}=V_q\Delta\sum_k\sum_b(q/2\,|\,p_i\,|\,b,q/2)(b,q/2\,|\,p_s\,|\,q/2)$$
$$\times T\sum_n\frac{2i\omega_n-E_1-E_2+i\omega_t}{\mathscr{D}(i\omega_n+i\omega_t)\mathscr{D}(i\omega_n)(i\omega_n-E_{b,q/2}-i\omega_\mu-E_0)}\,. \tag{45}$$

The sum over n in Eq. (45) can be written as two terms of the form

$$F=T\sum_n\frac{1}{(i\omega_n-\underline{b})(i\omega_n-\underline{a})(i\omega_n-\underline{c})(i\omega_n-\underline{d})}\,. \tag{46}$$

In both terms

$$\underline{b}=E_{b,q/2}-i\omega_\mu-E_0\,.$$

In one of them $\underline{a}=E_2$, $\underline{c}=E_2-i\omega_t$, and $\underline{d}=E_1-i\omega_t$. In the other term $\underline{a}=E_1$, $\underline{c}=E_1-i\omega_t$, and $\underline{d}=E_2$. F, as given by Eq. (46), can then be evaluated with the result

$$F=\frac{f_b-f_d}{(\underline{b}-\underline{a})(\underline{b}-\underline{c})(\underline{b}-\underline{d})}$$
$$+\frac{(f_d-f_c)(\underline{a}+\underline{c}-\underline{b}-\underline{d})}{(\underline{b}-\underline{a})(\underline{b}-\underline{c})(\underline{d}-\underline{a})(\underline{d}-\underline{c})}\,. \tag{47a}$$

Here f_b, f_d, and f_c $(=f_a)$ are Fermi functions for the energies $\underline{b}$, $\underline{d}$, and $\underline{c}$. The Matsubara frequencies $i\omega_\mu$ and $i\omega_t$ do not contribute to f_b, f_d, and f_c. Extracting the part of Eq. (47a) with two photon energy denominators (F_2) gives a total contribution from both F terms of

$$F_{2,\text{tot}}=\frac{-(f_1-f_2)}{E_1-E_2}\left[\frac{1}{(\underline{b}-E_1)^2}+\frac{1}{(\underline{b}-E_2)^2}\right]\,, \tag{47b}$$

where f_1 and f_2 are the Fermi functions

$$f_{1,2}=(e^{(E_{1,2}-E_0)/T}+1)^{-1} \tag{47c}$$

or

$$F_{2,\text{tot}}\approx\frac{-2(f_1-f_2)}{(E_1-E_2)(\underline{b}-E_{\text{av}})^2}\,, \tag{48a}$$

where

$$2E_{\text{av}}=E_1+E_2=E_k+E_{k+q}\,. \tag{48b}$$

After analytic continuation we set[16]

$$\underline{b}\rightarrow E_b-\omega_l-i\gamma_b\,, \tag{48c}$$

where

$$\omega_l=\tfrac{1}{2}(\omega_i+\omega_s) \tag{48d}$$

and

$$E_b\equiv E_{b,q/2}\,. \tag{48e}$$

In Eq. (48c) γ_b is the width of state $(b,q/2)$. A similar expression holds for

$$L_q^{(b)}+L_q^{(d)}=L_{-q}^{(b)}+L_{-q}^{(d)}\,.$$

Thus

$$L_q\cong-V_q\Delta P_{is}\sum_k\frac{f_1-f_2}{E_1-E_2}\,, \tag{49a}$$

where $E_{1,2}$ obey Eq. (44b) and where

$$P_{is}=2\sum_b(q/2\,|\,p_i\,|\,b,q/2)(b,q/2\,|\,p_s\,|\,q/2)$$
$$\times[(E_b-E_{\text{av}}-\omega_l-i\gamma_b)^{-2}$$
$$+(E_b-E_{\text{av}}+\omega_l+i\gamma_b)^{-2}]\,. \tag{49b}$$

Upon comparison of Eqs. (49a) and (49b) with the one-band weak CDW result Eqs. (25a)–(25d) and (24b) we see that the main change is the substitution of

$$\frac{f_1-f_2}{E_1-E_2} \tag{49c}$$

for

$$\frac{f_k-f_{k+q}}{E_k-E_{k+q}} \tag{49d}$$

In the case of the $2H$ layered compounds we must use a two-band, two-phonon-mode model, and there are four coupled components of the electron Green's function, but only two of them are strongly coupled if interlayer interactions are weak.

F. The case of one dimension

Within mean-field theory the self-consistency condition Eq. (11) gives, using Eqs. (9b), (8), and (42a) and (42b) the "gap" equation

$$1=\frac{-2V_q^2}{\omega_q^0}\sum_k\frac{f_1-f_2}{E_1-E_2}\ . \tag{50a}$$

In one dimension this is BCS-like and gives for linear $E(k)$ near the Fermi energy:

$$\Delta(T=0)=\Delta_0=E_B e^{-\omega_q^0 E_B/g^2}\ , \tag{50b}$$

where E_B (assumed $\gg\Delta_0$) is the width of the band and where

$$g=\sqrt{N}\,V_q\ . \tag{50c}$$

Integrating Eq. (49a) in the one-dimensional case gives

$$\frac{1}{N}\sum_k\frac{f_1-f_2}{E_1-E_2}=\frac{1}{E_B}\ln(E_B/\Delta)\ , \tag{51a}$$

and thus

$$L_q=-\Delta_0 P_{is}\sqrt{N}\left[\frac{g}{E_B}\ln\frac{E_B}{\Delta_0}\right]\ . \tag{51b}$$

If the mean-field gap equation (50a) holds, then for any dimension

$$L_q=-\frac{\Delta_0 P_{is}\sqrt{N}}{2}\frac{\omega_q^0}{g}\ . \tag{52}$$

Equations (50)–(52) may also describe Raman scattering in systems such as $K_2Pt(CN)_4\,Br_{0.3}\cdot 3H_2O$ (known as KCP)[37] where one-dimensional Fermi-surface "nesting" is possible even in a three-dimensional material.[38–40] A low-frequency Raman study by Steigmeier *et al.*[41] found a line of A_1 symmetry at about 44 cm^{-1}. This was interpreted[41] as the amplitude mode of the CDW associated with an incomplete distortion having a new unit cell $2a\times 2a\times 6.7\ (c/2)$, where $c/2$ is the average spacing between Pt atoms along the "one-dimensional" chains.[42] There is no long-range order transverse to the c axis[42]; one should think of nearly frozen regions of fluctuations into a distorted phase from which CDW phonon modes can be observed.

The band structure of KCP along the Pt chain directions is s-like and free-electron-like near the Fermi energy,[43] and the resulting phonon softening in the normal phase has a very sharp Kohn anomaly. Thus the CDW is of the original Peierls type and not one associated with narrow d band as with the transition-model dichalcogenides.

G. Role of anharmonicity for strong CDW case

McMillan has argued that a BCS-like gap equation is invalid in the transition-metal dichalcogenides, where phonons over a large region of q space are soft.[21] Anharmonic coupling among these modes then leads to a phonon contribution to the entropy that dominates the electronic contribution (due to excitations across the CDW gap) implicit in Eq. (50a). A simplified version of McMillan's argument has been given by Inglesfield,[44] who points out that quartic anharmonicity will stabilize the normal phase to temperatures below that given by the harmonic mean-field theory [see Eq. (14)]. McMillan performed numerical calculations for $2H$-$TaSe_2$,[21] taking anharmonic parameters from experiment and found a value for the gap Δ about 6 times larger than implied by Eq. (50b). He did not use the correct Landau parameterization allowed by symmetry[24–28] and thus his numerical results may be in error.

The anharmonic phonon entropy model[21,44] was inspired in part by infrared data that suggest a large CDW gap $2\Delta_0$ of about 0.25 eV for $2H$-$TaSe_2$.[45] Other optical data and calculations support a gap of this magnitude[34] but this interpretation of the data has not been universally accepted.[46]

If anharmonicity does increase Δ_0, Eq. (51b) shows that in one dimension there will be a relatively weak (logarithmic) decrease in the Raman amplitude. In higher dimensions this decrease will be even weaker than logarithmic.

H. Remark about $1T$ polytypes

The present theory will be inadequate to describe the very strong distortions found in the $1T$ transition-metal dichalcogenides. The commensurate ($1T_3$) phase of $1T$-TaS$_2$ is a semiconductor.[1] An interesting model for this state has been proposed by Fazekas and Tosatti.[47] They argue that 12 of the 13 conduction electrons in each distorted 13-atom cluster will be paired in covalent bonds.[44] The remaining electron undergoes localization when the $1T_3$ phase is formed, giving a Mott insulator. One should then regard the cluster as a quasimolecule, find its normal vibrational modes, and their coupling to the interband electronic excitations of the cluster. Such an approach is needed to explain the multiplicity of sharp, strong Raman lines observed in this phase.[12] In the higher-temperature incommensurate phases the strongest feature is a single, rather broad band,[12] and the calculation of the last section might serve as the start for a microscopic theory.

IV. CONCLUSIONS

In the weak CDW state the part of the Raman amplitude that is linear in the CDW order parameter is closely related to the intralayer phonon self-energy in a metastable normal state at temperature $T < T_0$, and only amplitude modes will have appreciable intensity. In $2H$-TaSe$_2$ the observed, rather strong intensity of phase modes is due to third- and fourth-order intralayer anharmonicity and closely related second- and third-order terms in the Raman amplitude. In stronger CDW systems an increasing CDW gap increases the denominators of the scattering amplitudes and therefore reduces them somewhat, but qualitative results should be similar to the weak CDW case. For ultrastrong CDW's which produce a metal-insulator transition, the present theory will be inadequate.

Note added in proof. In a recent paper N. Nagaosa and E. Hanamura [Solid State Commun. 41, 809 (1982)] have also discussed Raman scattering in $2H$-TaSe$_2$ and $2H$-NbSe$_2$ using a Landau theory with third-order coupling coefficients. Although they used an earlier version of the Landau theory[21] and assumed an hexagonal commensurate state, they reached some of the same conclusions reached here, namely that intralayer anharmonicity hybridizes E amplitude and E phase modes but not the corresponding A modes.

ACKNOWLEDGMENTS

The author thanks W. L. McMillan for many helpful discussions and N. Nagaosa for a useful conversation. This research was supported by the National Science Foundation under the MRL Grant DMR-80-20250.

APPENDIX: LANDAU THEORY OF CDW PHONONS IN $2H$-TaSe$_2$

The free energy per unit area per two-layer section may be written[26]

$$F = F_1 + F_2 + F_{12} , \tag{A1a}$$

where the free energy for layer l is

$$F_l = \sum_{j=1}^{3} \Bigg[A \,|\, \psi_{lj} \,|^2 + B \left| \left(i \frac{\partial}{\partial x_{\| j}} + \partial \right) \psi_{lj} \right|^2 + C \left| \frac{\partial \psi_{lj}}{\partial x_{\perp j}} \right|^2 + G \,|\, \psi_{lj} \,|^4 + K \,|\, \psi_{lj} \psi_{lj+1} \,|^2$$
$$- \mathrm{Re} \left(\tfrac{1}{3} D_l \psi_{l1} \psi_{l2} \psi_{l3} + E_l \psi_{lj}^3 + M_l \psi_{lj}^2 \psi_{lj+1}^* \psi_{lj+2}^* \right) \Bigg] , \tag{A1b}$$

and the interlayer term is

$$F_{12} = 2\, \mathrm{Re} \sum_j L \psi_{1j}^* \psi_{2j} . \tag{A1c}$$

If the phase ϕ_0 in Eq. (18) is $-\pi/2$, we may take the CDW displacements in Eq. (A1b) as proportional to

$$\vec{\nabla}_{\vec{R}} \psi_{lj} e^{i \vec{q}_j \cdot \vec{R}} .$$

Thus we may assume that the equilibrium order parameters obey

$$\psi_{1j}=\epsilon\exp[-i\phi_1(q_j)]\ , \tag{A2a}$$

$$\psi_{2j}=\epsilon\exp[i\phi_2(q_j)]\ . \tag{A2b}$$

The phases obey[26]

$$\phi_1(q_j)=2\pi n_j/3+\theta\ , \tag{A2c}$$

$$\phi_2(q_j)=2\pi\bar{n}_j/3+\theta\ , \tag{A2d}$$

where n_j and $\bar{n}_j$ are integers. In Eq. (A1b), D_l, E_l, and M_l are complex. We write

$$D_1=|D|e^{-i\phi_D}\ , \tag{A3a}$$

etc. Invariance of F under the inversion operation, which sends ψ_{1j} into ψ_{2j}^*, requires that

$$D_2=D_1^*\ , \tag{A3b}$$

etc. $F^{(0)}$, the zero-order value for F is obtained by substituting Eqs. (A2) into Eqs. (A3). For layer 1 we obtain

$$F_1^{(0)}=3(A+B\delta^2)\epsilon^2+3(G+K)\epsilon^4$$
$$+3\epsilon^4\,\mathrm{Re}\widetilde{M}-\epsilon^3\,\mathrm{Re}(\widetilde{D}+3\widetilde{E})\ , \tag{A4a}$$

where

$$\widetilde{M}=|M|\exp[i(-\phi_M+2\pi m/3)]\ , \tag{A4b}$$

$$\widetilde{D}=|D|\exp[-i(\phi_D+2\pi m/3+3\theta)]\ , \tag{A4c}$$

$$\widetilde{E}=|E|\exp[-i(\phi_E+3\theta)]\ , \tag{A4d}$$

with

$$m=n_1+n_2+n_3\ , \tag{A4e}$$

modulo 3. We also introduce

$$\bar{m}=\bar{n}_1+\bar{n}_2+\bar{n}_3\ , \tag{A4f}$$

modulo 3, and find that $F_2^{(0)}$ is given by $F_1^{(0)}$ with m replaced by $\bar{m}$ in Eqs. (A4b) and (A4c).

We neglect $F_{12}^{(0)}$ and minimize $F_1^{(0)}$ with respect to θ. This gives

$$\mathrm{Im}(\widetilde{D}+3\widetilde{E})=0\ , \tag{A5a}$$

which is independent of the amplitude ϵ. We can then write

$$\mathrm{Re}(\widetilde{D}+3\widetilde{E})=\Gamma\ , \tag{A5b}$$

where

$$\Gamma=|\widetilde{D}+3\widetilde{E}|\ . \tag{A5c}$$

Minimization of (A4a) with respect to ϵ then gives

$$2(A+B\delta^2)+4(G+K)\epsilon^2-\Gamma\epsilon-4\epsilon^2\,\mathrm{Re}\widetilde{M}=0\ . \tag{A5d}$$

The equilibrium value of m will require knowledge of the Landau parameters $|M|$, $|D|$, ϕ_M, and ϕ_D. Available ^{77}Se NMR results of Suits *et al.*[48] and unpublished ^{181}Ta Mössbauer data by Pfeiffer favor $m=\bar{m}=1$.[26] The values of n_j and $\bar{n}_j$ will then be those that minimize the zero-order interlayer term

$$F_{12}^{(0)}=2|L|\epsilon^2$$
$$\times\sum_j\cos[2\theta+2\pi(n_j+\bar{n}_j)/3-\phi_L]\ . \tag{A6c}$$

McMillan has argued that $\phi_L\approx 0$ and that θ can be selected so that $F_{12}^{(0)}$ is minimized for $m=1$, $\bar{m}=1$ states with parameters such as[28]

$$(n_1n_2n_3)=(100)\ , \tag{A7a}$$

$$(\bar{n}_1\bar{n}_2\bar{n}_3)=(010)\ . \tag{A7b}$$

This state, denoted by McMillan as $\beta\beta 1(100;010)$, has inversion symmetry about the midpoint between two Ta atoms at $\vec{d}=\vec{a}_2+\vec{a}_3\ (=-\vec{a}_1)$, which is parallel to $\vec{q}_2-\vec{q}_1$. It therefore obeys Eqs. (19a)–(19d) with

$$(m_1m_2m_3)=(011)\ . \tag{A7c}$$

The orthorhombic axes are along $\vec{d}$ and $\vec{q}_3$.

To Eqs. (A2a) and (A2b) we now add the fluctuations

$$\delta\psi_{1j}=(\alpha_j-i\beta_j)\epsilon\exp[-i\phi_1(q_j)]\ , \tag{A8a}$$

$$\delta\psi_{2j}=(\bar{\alpha}_j+i\bar{\beta}_j)\epsilon\exp[i\phi_2(q_j)]\ . \tag{A8b}$$

In the notation of Eqs. (33) we have, for instance,

$$\alpha_j=\frac{u_0}{\epsilon\sqrt{N}}(b_{\eta 1}^{q}+b_{\eta 1}^{q\dagger})\ \text{ for } q=q_j\ , \tag{A8c}$$

and

$$\beta_j=\frac{u_0}{\epsilon\sqrt{N}}(b_{\phi 1}^{q}+b_{\phi 1}^{q\dagger})\ \text{ for } q=q_j\ . \tag{A8d}$$

We now consider $F^{(2)}$, the second-order terms in $\delta\psi_{lj}$. We transform α_j and β_j into symmetry coordinates α_γ and β_γ, where $\gamma=A$, E_1, and E_2, by transformations identical to Eqs. (29a)–(29c). We introduce the parameter ρ^*, which equals the effective mass M^* divided by the area of a unit cell and find:

$$2\frac{F_1^{(2)}}{\rho^*}=(\omega_\eta^A)^2\alpha_A^2+(\omega_{\eta 0}^E)^2(\alpha_{E1}^2+\alpha_{E2}^2)$$
$$+(\omega_\phi^A)^2\beta_A^2+(\omega_{\phi 0}^E)^2(\beta_{E1}^2+\beta_{E2}^2)$$
$$+(\omega_{\eta\phi}^E)^2(\alpha_{E1}\beta_{E1}+\alpha_{E2}\beta_{E2})\ , \tag{A9a}$$

where

$$\rho^*(\omega_\eta^A)^2=8\epsilon^2(G+K-\mathrm{Re}\widetilde{M})-\Gamma\epsilon\,, \tag{A9b}$$

$$\rho^*(\omega_\phi^A)^2=3\Gamma\epsilon\,, \tag{A9c}$$

$$\rho^*(\omega_{\eta 0}^E)^2=(8G-4K)\epsilon^2+2\Gamma\epsilon+\epsilon\,\mathrm{Re}(7\widetilde{M}\epsilon-9\widetilde{E})$$

$$\rho^*(\omega_{\phi 0}^E)^2=9\epsilon\,\mathrm{Re}(\epsilon\widetilde{M}+\widetilde{E})\,, \tag{A9d}$$

$$\rho^*(\omega_{\eta\phi}^E)^2=-6\epsilon\,\mathrm{Im}(\epsilon\widetilde{M}+3\widetilde{E})\,. \tag{A9e}$$

Equations (A5) have been used to obtain Eqs. (A9b)–(A9e). These results agree with those of Holy *et al.*[5] when their restricted set of Landau parameters are used and with Rice,[25] if his restriction to phase modes only is maintained. Note that no $\alpha_A\beta_A$ cross term appears in Eq. (A9a). Its coefficient, $-2\,\mathrm{Im}(\widetilde{D}+3\widetilde{E})$, vanishes by Eq. (A5a).

The E amplitude and E phase modes are seen to mix. The amount of mixing is governed by the parameter

$$\tan\delta\equiv\frac{(\omega_{\eta\phi}^E)^2}{(\omega_{\phi 0}^E)^2-(\omega_{\eta 0}^E)^2}=\frac{-3\,\mathrm{Im}(\epsilon\widetilde{M}+3\widetilde{E})}{\epsilon(2K-4G+\mathrm{Re}\widetilde{M})+9\,\mathrm{Re}\widetilde{E}-\Gamma}\,. \tag{A10}$$

Note that this has a finite limit as $\epsilon\rightarrow 0$.

The Raman data suggest that the higher-frequency E mode is the phase mode, since it has the weaker intensity[3,5,9,36] and rapidly weakens as the temperature is raised.[3] Thus we assume that $\omega_{\phi 0}^E>\omega_{\eta 0}^E$ and find new phaselike and amplitude-like modes whose frequencies obey

$$\omega_\eta^{E^2}+\omega_\phi^{E^2}=\omega_{\eta 0}^{E^2}+\omega_{\phi 0}^{E^2}\,, \tag{A11a}$$

and

$$(\omega_\phi^E)^2-(\omega_\eta^E)^2=\{[(\omega_{\phi 0}^E)^2-(\omega_{\eta 0}^E)^2]^2+(\omega_{\eta\phi}^E)^4\}^{1/2}\,, \tag{A11b}$$

and whose coordinates β'_{Ej} and α'_{Ej} are given by the transformation

$$\beta'_{EJ}=\beta_{Ej}\cos\frac{\delta}{2}+\alpha_{Ej}\sin\frac{\delta}{2}\,, \tag{A11c}$$

$$\alpha'_{Ej}=-\beta_{Ej}\sin\frac{\delta}{2}+\alpha_{Ej}\cos\frac{\delta}{2}\,. \tag{A11d}$$

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