Raman Spectroscopy of Soft Modes at the Charge-Density-Wave Phase Transition in $2H$-NbSe$_2$

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The Raman spectra of the layer-structure compounds $2H$-NbSe$_2$ and $2H$-TaSe$_2$ have been measured between 2 and 300 K. A low-energy peak in the Raman spectrum is found to soften at the charge-density-wave phase transition. This peak is attributed to the charge-density-wave amplitude mode. The intensity and energy of this soft mode have been successfully compared with mean-field treatments of the charge-density-wave phase transition.

Charge-density waves (CDW's) occur in many of the metallic layer-structure transition-metal dichalcogenides.[1-4] In $2H$-NbSe$_2$, in the absence of a CDW, all the Nb ions occupy symmetrically equivalent sites. For $T < T_c = 33.5$ K, an incommensurate charge-density wave (ICDW) (i.e., a periodic modulation of conduction electron density whose wavelength is not a simple multiple of the lattice constant) is present. The variation in conduction electron density at Nb ion sites for $T \ll T_c$ is estimated to be $\leq 9\%$.[5] The conduction electron ICDW is accompanied by a periodic lattice distortion, also incommensurate with the undistorted lattice. We have previously shown that this reduction in the long-range order of the crystal structure and consequent reduction in the size of the first Brillouin zone are accompanied by dramatic changes in the Raman spectra.[6]

The transition between the undistorted state and the ICDW state is a second-order displacive phase transition[4] with a soft, Raman-active (for $T < T_c$) phonon mode whose eigenvector describes the lattice distortion at the phase transition. This mode corresponds to a harmonic variation of the amplitude of the ICDW lattice distortion and is commonly known as the amplitude mode.[7] The intensity of the amplitude mode and its energy have a characteristic dependence on the reduced temperature $t = (T_c - T)/T_c$ of the sample. Furthermore, it has been shown that this energy is simply related to the magnitude of the electron-photon coupling constant and to the temperature-dependent order parameter associated with the phase transition.[7] The small magnitude of the lattice distortion and the absence of a first-order incommensurate-to-commensurate CDW phase transition in $2H$-NbSe$_2$ suggests that existing theories of second-order phase transition, based on power-series expansions of the free energy, might adequately treat the ICDW phase transition in this material. We have identified low-energy, temperature-dependent Raman scattering in $2H$-NbSe$_2$ for $T < T_c$ with the ICDW amplitude mode and show below that our results are consistent with mean-field theories. Steigmeir *et al.*[8] have observed Raman scattering from an amplitude mode of the charge-density wave in the linear-chain compound $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ (KCP). In contrast to our results and the predictions of mean-field theories, the energy of the amplitude mode in KCP is only weakly temperature-dependent. This is probably due to the fact that the ~100-K phase transition is not a simple CDW phase transition and to the inability of mean-field theories to describe quasi-one-dimensional systems in which fluctuations are important at all temperatures.[8]

The samples studied were all freshly cleaved single crystals, grown by iodine vapor transport from pre-reacted powder. They were characterized by x-ray diffraction and transport measurements. For measurement of the Raman spectra the samples were mounted on copper disks which were attached to a solid copper block. The temperature of the copper block was measured with a platinum resistance thermometer. Optical measurements were made with the sample either immersed in superfluid He or in cold gaseous He. The Raman spectra were measured in a backscattering geometry, using a variety of Ar and Kr ion laser lines. Because of sample geometry, both incident and scattered light polarizations were restricted to the crystal basal plane for all measurements. Sample heating was minimized by limiting incident light power to 60 mW or less and by focusing the laser beam to a line on the sample using a cylindrical lens. Analysis of the temperature dependence of the resulting $2H$-NbSe$_2$ spectra near the 33.5-K phase transition suggests that heating effects were $\lesssim 2-3$ K.

In Fig. 1, we show parallel-polarization (i.e., polarization of incident and scattered light parallel) Raman spectra of $2H$-NbSe$_2$ at a number of temperatures both above and below the 33.5-K transition from the undistorted to the ICDW state.

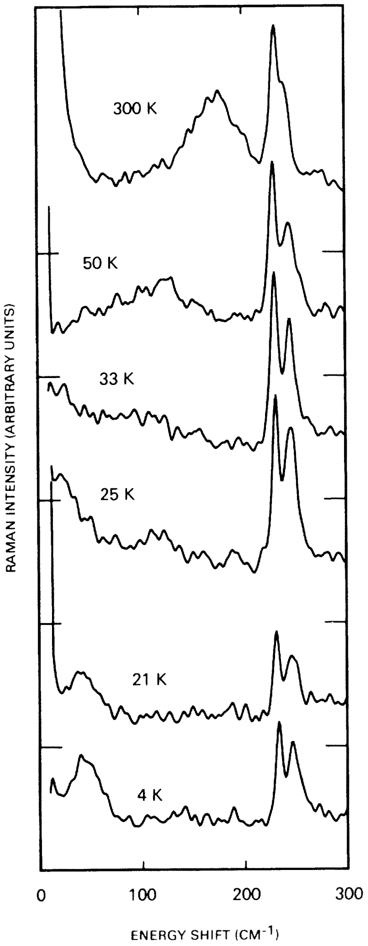

FIG. 1. Raman spectra of $2H$-NbSe$_2$ above and below the 33.5-K undistorted-to-ICDW phase transition. The spectra were excited using 30 mW of power at 5145 Å.

The room-temperature spectrum is similar to that previously reported.[9] It is dominated by sharp lines with A_{1g} symmetry (observed only in the parallel-polarization scattering configuration in the basal plane) at 230 cm^{-1} and $E_{2g}{}^1$ symmetry (parallel and crossed polarizations) at 238 cm^{-1} and a broad maximum centered at ≈ 180 cm^{-1} with full width at half-maximum ≈ 50 cm^{-1}. As the temperature of the sample is decreased, the 238-cm^{-1} line moves to higher energy and increases in strength, relative to the 230-cm^{-1} line. The broad band changes its shape, shifts to lower energies, and first increases and then decreases in relative intensity (again compared to the 230-cm^{-1} line). For T just above the ICDW transition the broad peak is no longer observable. Below the ICDW phase transition, a number of new lines appear and the $E_{2g}{}^1$ symmetry line, now at about 245 cm^{-1}, broadens significantly, with a width at 4 K almost double that of the A_{1g} line. Of the new structures, the most prominent are a weak, sharp line at 186 cm^{-1} and a strong broad line (width >20 cm^{-1}) at low energies. The low-energy mode is observed only in the parallel-polarization (A_{1g}) scattering geometry. Both the energy and intensity of this broad, low-energy line decrease rapidly as the temperature approaches T_c from below.

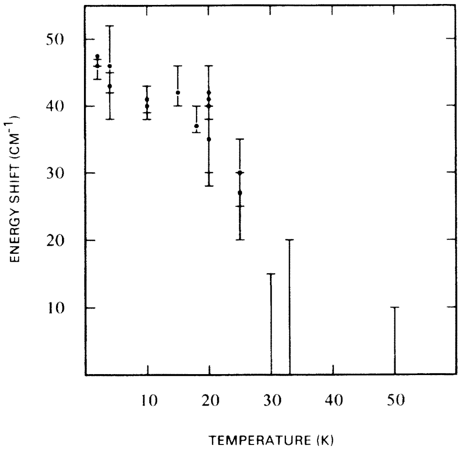

FIG. 2. Temperature dependence of the energy of the A_{1g} soft mode in the ICDW phase.

In Fig. 2 we show the temperature dependence of the energy of the broad, low-lying mode. The identification of the ICDW to undistorted-state phase transition as a second-order structural phase transition and the softening of the Raman-active mode at the transition temperature is by itself evidence for the identification of this mode as the amplitude mode. In addition, mean-field theory supports this identification. Rice and coworkers,[7] using a mean-field theory, have shown that the energy of the amplitude mode of a charge-density wave is given by

$$\omega(T) = 1.4\Lambda^{1/2}\omega_0 t^{1/2}, \tag{1}$$

where Λ is the electron-phonon coupling constant, t is the reduced temperature, and ω_0 is the unscreened, or high-temperature phonon frequency. Our data are consistent with the temperature dependence given by Eq. (1); and we take this to be further evidence for the identification of the soft mode as the ICDW amplitude mode. If we take $T_c = 33.5$ K and $\omega_0 = 85$ cm^{-1}, we can derive from our data a result $\Lambda = 0.17$.[10] This relatively small value of Λ[11] can be understood if we consider the definition of the electron-phonon coupling constant,

$$\Lambda = N(0)g^2(0)/\omega_0, \tag{2}$$

where $g(0)$ is the electron-phonon matrix element for electronic states at the Fermi surface which are connected by phonons of energy ω_0 and $N(0)$ is the density of states of these electrons and holes. Since the charge-density-wave transition in $2H$-NbSe$_2$ involves only a small portion of the Fermi surface, $N(0)$ in this case refers only to this fraction of the density of states.

As noted above, the intensity of the amplitude-mode Raman scattering is also strongly temperature-dependent, vanishing as T_c is approached from below. Petzelt and Dvořák[12] have recently given a group-theoretical treatment of the behavior of soft-mode energies and intensities at structural phase transitions. They find that the intensity of a soft mode which is not Raman-active in the undistorted phase can in general be accounted for by a Raman tensor α_{ij} related to the order parameter δ by an expression of the form

$$\alpha_{ij} \propto \delta^q, \tag{3}$$

with q an integer and equal to 1 or 2 in all of the cases surveyed in the review.

We can determine the exponent q in Eq. (3) by analysis of the relationship of Raman intensity to either temperature or soft-mode energy in the ICDW phase. We have chosen the latter approach in order to minimize the effects of temperature uncertainty on the analysis. The Raman intensity is related to the Raman tensor by

$$I = B|\alpha_{ij}|^2[n(\omega, T) + 1]/\omega, \tag{4}$$

where $n(\omega, T)$ is the Bose-Einstein distribution function evaluated at mode energy ω and temperature T, and B is a proportionality constant. The form of the relationship between α_{ij} and δ given in Eq. (3) is assumed to be valid and the energy dependence of α_{ij} is determined by observing that Fig. 2 indicates that $\omega \propto \delta$. With these assumptions, we have calculated I as a function of ω for several different integral values of the exponent q. We find that the data are best fitted by $q = 2$, shown by the solid line in Fig. 3.

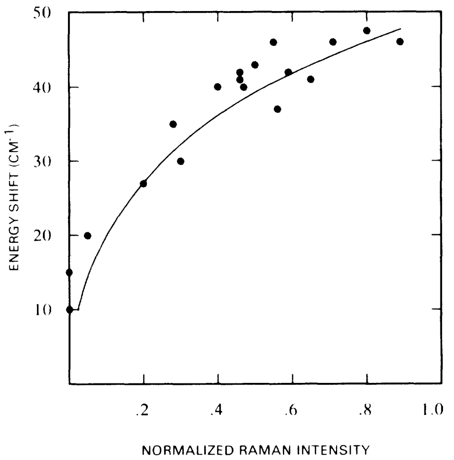

FIG. 3. Variation of the intensity of the soft mode with mode energy in the ICDW phase. The solid line corresponds to $q = 2$ in Eq. (3).

The soft phonon mode observed below the ICDW transition is Raman-inactive above the transition since it corresponds to the excitation of a non-zone-center longitudinal acoustic (LA) phonon. However, substantial changes in the Raman spectra with temperatures are observed above T_c. As we have noted above and shown in Fig. 1, with lowering temperature (but remaining in the undistorted phase) the broad line shifts to lower energies; at T_c its intensity vanishes. Moncton, Axe, and Di Salvo[3] have observed a softening of the Σ-branch phonon dispersion curves of $2H$-NbSe$_2$ as T_c is approached from above. The temperature dependence of the broad-line Raman scattering we find above T_c, compared with the results of Moncton, Axe, and Di Salvo leads us to associate this broad line with scattering by two LA phonons on the Σ branch from opposite sides of the zone.

We have also studied the temperature dependence of Raman scattering from $2H$-TaSe$_2$. This material is isostructural to $2H$-NbSe$_2$ and has a transition to an ICDW at 122 K, followed by a second transition to a commensurate CDW at 90 K. This second transition makes $2H$-TaSe$_2$ less amenable to detailed comparisons with existing theories. However the results are in qualitative agreement with our observations on $2H$-NbSe$_2$ and therefore support the analysis given above. The ICDW–to–commensurate-CDW transition at 90 K makes it impossible to determine $\omega(0)$ and therefore impossible to use Eq. (1) to calculate Λ for $2H$-TaSe$_2$.

In conclusion, we have used Raman spectroscopy to study the transitions from the normal undistorted states to the ICDW states of both $2H$-NbSe$_2$ and $2H$-TaSe$_2$. We have observed substantial temperature-dependent effects both above and below T_c. We have identified a soft mode of the low-temperature phase which corresponds to an amplitude excitation of the CDW. In $2H$-NbSe$_2$, which we have studied more thoroughly, we have been able to obtain an estimate of the magnitude of the electron-phonon coupling.

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[10] The value of 85 cm^{-1} is based on the neutron scattering data of Moncton, Axe, and Di Salvo (Ref. 3). The LA phonon dispersion of $2H$-NbSe$_2$ at 300 K shows only a very weak dip near the CDW wave vector and only a very weak temperature dependence. This is consistent with the assumption that any Kohn anomaly is quite weak at 300 K. Furthermore, we note that our choice of $\omega_0 = 85$ cm^{-1} really represents the smallest likely value; any large value would result in even lower estimate for the value of Λ, consistent with the fact that only a small fraction of the Fermi surface is affected by the CDW transition.

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Pronounced Isotope Effect in the Superconductivity of HfV$_2$ Containing Hydrogen (Deuterium)*

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Superconducting transition temperatures of HfV$_2$H$_x$ and HfV$_2$D$_x$ have been measured in the composition ranges $x = 0-1.5$ and $x = 0-1.0$, respectively. Hydrogen or deuterium absorption is found to decrease T_c of HfV$_2$. Pronounced isotope effects have been observed. At $x = 1$, hydrogen absorption reduces T_c by 4.8 K while deuterium absorption reduces T_c by 6.9 K with respect to HfV$_2$.

Superconductivity in metal-hydrogen systems has recently been a subject of considerable interest due to the possibility of finding high T_c in these materials via an attractive pairing interaction arising from the high-frequency vibrational modes of the proton lattice. Detailed studies have so far been carried out on the hydrides and deuterides of thorium[1] and palladium.[2-5]

It is interesting to note that although Pd itself is not superconducting, Pd-H and Pd-D exhibit T_c values as high as 9 and 11 K, respectively.[3-5] Moreover, in Pd-Cu-H, Pd-Ag-H, and Pd-Au-H systems, high T_c values of 16.6, 15.6, and 13.6 K, respectively, could be attained.[6] Since, in the absence of hydrogen, these alloys are nonsuperconducting, it is evident that the appearance of superconductivity in the hydrides of Pd and Pd–noble-metal alloys is not just a result of the quenching of spin fluctuations as was supposed earlier.[7] It seems to have its origin[8,9] in the enhanced pairing interaction arising from the high-frequency optic phonon modes[10] associated with the proton (or deuteron) lattice.

Another interesting feature is the discovery that Th$_4$H(D)$_{15}$ exhibits no detectable isotope effect[1] while Pd-H(D) exhibits a pronounced reverse isotope effect[3-5] (T_c for PdH ~ 9 K and for PdD ~ 11 K). The reverse isotope effect in PdH(D) has been explained separately on two different models. The first model[8] involves the influence of the optic modes on the electron-phonon coupling in PdH and PdD. The second model[4] attributes the effect to the difference in electronic structure due to the H atom spending more time in the proximity of the Pd atom than the D atom.

In view of these interesting features, further studies are needed to understand the nature of superconductivity in metal-hydrogen systems. The hydrides of the cubic Laves ($C15$) phase alloys Hf$_x$Zr$_{1-x}$V$_2$ are well suited for a detailed investigation because of their high T_c and H_{c2} values[11-15] [$T_c = 8.6$ to 10.1 K, $H_{c2}(4.2) = 100$ to 230 kOe] and ability to absorb large quantities of hydrogen at room temperature and moderate pres-