where the curve is negative represent an excess in electronic states at the surface. This calculated state-density difference is seen to be quite similar to those shown in Fig. 4(b). The latter are the measured effect on the photoemission intensity of the chemisorption of two different adsorbates.[5] The highly localized character of the wave functions of these surface states (Fig. 2) is consistent with the present interpretation of their high reactivity with adsorbates.

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Raman Spectroscopy of the Charge-Density-Wave State in TaS_3

J. C. Tsang, C. Hermann,[a] and M. W. Shafer
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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Raman spectroscopy has been used to study the quasi-one-dimensional charge-density-wave (CDW) compound, TaS_3. We determine for the first time both the temperature dependence of the CDW order parameter and the magnitude of the electronic gap $2\Delta(T)$ opened by the CDW at the Fermi surface. The transition to the CDW state appears to be continuous; our value of $2\Delta(0) \simeq 530$ cm^{-1} is in agreement with both theory and transport measurements.

Sambongi *et al.*[1] have reported a charge-density-wave- (CDW-) induced semiconductor-to-metal transition and superlattice in the quasi-one-dimensional compound TaS_3 for $T < 220$ K. Information concerning the phononlike excitations of the CDW states and the dynamics of the phase transitions from the CDW states has been obtained from Raman studies of layered-structure compounds.[2-4] We report here the first study of the Raman spectrum of TaS_3. We observe temperature-dependent shifts in the frequencies of the normal-state optic phonons which allow us to measure the temperature dependence of the CDW order parameter η since these shifts are proportional to η^2.[5] We have also been able to obtain, from the temperature dependence of the phonon linewidths, the magnitude of the electronic gap introduced at the Fermi surface by the CDW. While the existence of a gap at the Fermi energy E_F in the electronic structure of the CDW state is accepted, there has

been very little direct spectroscopic evidence for it.[6] In this work, we show for the first time that Raman spectroscopy can measure the electronic gap $2\Delta(T)$ created by the CDW.

We measure the CDW-induced gap through its effect on the linewidths of our Raman-active phonons. Axe and Shirane[7] observed in Nb_3Sn that the superconducting gap 2Δ has a measurable effect on the linewidths of phonons whose energies are less than 2Δ. For temperatures greater than the transition temperature T_c, a phonon of energy ω_i can relax through the excitation of an electron whose energy is within ω_i of E_F. However, for $T < T_c$, if the phonon energy is less than $2\Delta(T)$, then this relaxation channel no longer exists and the phonon lifetime will increase, producing a narrowing of the Raman line. An analogous effect should be present in a CDW system where a gap is also opened at the Fermi surface. We indeed observe distinctive increases in the linewidths of the Raman-active phonons as the temperature approaches T_c for $T < T_c$.

Our measurements were made on multiple crystals of TaS_3. The samples were prepared by reacting Ta metal powder with elemental S and were crystallized in a quartz tube by either iodine or thermal transport for $T \simeq 500$°C. The crystals are hairlike with dimensions of the order of 1 cm $\times 10$ μm $\times 1$ μm. Electron diffraction patterns show a superlattice at 77 K identical to that reported by Sambongi *et al.*[1] Both pressed pellets and arrays of crystals were measured. The spectra were obtained in the backscattering geometry using the lines from an Ar^+ or a Kr^+ laser. The samples were studied in a helium gas ambient with a variable-temperature Dewar and the temperature of the sample holder was measured by a Si diode. The incident laser power was held below 50 mW and a cylindrical lens was used. For these conditions, temperature stability was of the order of 1 K and laser heating was less than 10 K in the pressed pellets. Temperature uncertainties as large as 50 K were observed in measurements on the arrays of single crystals where the samples were often in poor contact with the holder.

The Raman spectra of TaS_3 at 300 and 10 K for frequency shifts between 150 and 600 cm^{-1} are shown in Fig. 1. A detailed disucssion of the spectrum, its polarization properties, and its relationship to the crystallographic structure of TaS_3 will be presented in a forthcoming paper.[8] In this Letter, we shall only consider the temperature dependence of three lines, the lines at 283, 405, and 496 cm^{-1}. In what follows, we shall identify them by their wave numbers (in cm^{-1}) at 300 K.

In Fig. 2, we show the temperature dependence of the frequency of the 283-cm^{-1} line. This line shifts weakly to higher energies with decreasing temperature for $220 < T < 300$ K and then shifts by about 13.5 cm^{-1} for $T < 220$ K. The solid line represents a temperature dependence of the form

$$\omega(T) = 284 + 13.5(1 - T/220)^{1/2}, \quad 0 < T < 220 \text{ K},$$

$$\omega(T) = 287 - 0.012T, \quad 220 < T < 300 \text{ K}.$$

The other Raman lines of TaS_3 show similar shifts in position with temperature. The dependence of ω on temperature allows us to use it as an independent check on the sample temperature. In Fig. 3, we show the temperature dependence

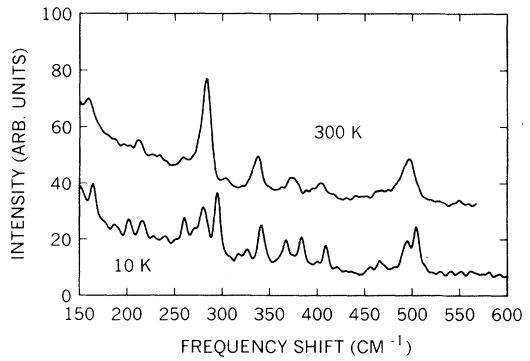

FIG. 1. The Raman spectra of TaS_3 at 300 and 10 K under 5145-Å laser excitation. The polarization of the scattered light is unanalyzed.

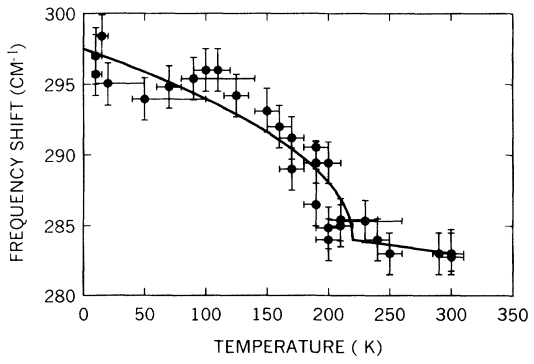

FIG. 2. The temperature dependence of the frequency of the strong line at 283 cm^{-1} in the Raman spectrum of TaS_3. The CDW transition in TaS_3 is at 220 K. Points with large temperature uncertainties correspond to data taken on loose arrays of fibers.

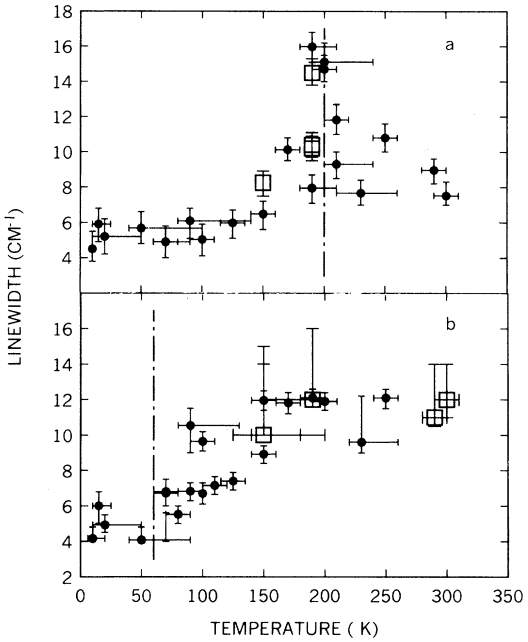

FIG. 3. The temperature dependence of the full width at half-maximum of the Raman line at (a) 283 cm^{-1} and (b) 496 cm^{-1}. The large boxes represent data taken on samples for which the position of the 283-cm^{-1} line is used to obtain the sample temperature. The vertical lines show the temperatures at which the phonon energy equals $2\Delta(T)$.

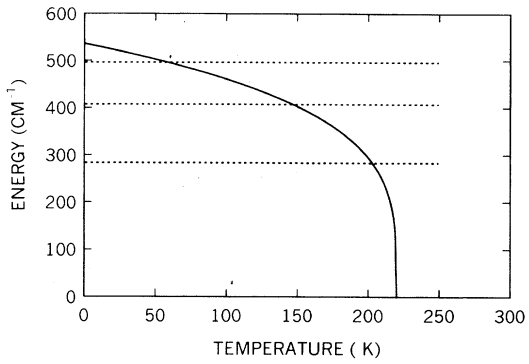

FIG. 4. The magnitude of the CDW gap $2\Delta(T)$ for $0 < T < 250$ K. Broken lines show the nominal positions of the three phonons discussed.

of the linewidths of two of the Raman lines of TaS_3. These widths and the error bars are obtained from Lorentzian fits to our experimental results. The width of the 283-cm^{-1} line shows no appreciable changes for $T < 100$ K and does not begin to increase until $T > 175$ K. In contrast, the width of the 496-cm^{-1} line begins to increase rapidly for $T < 80$ K. The uncertainties in its width near 200 K arise from the weakness of this line and the proximity of other structures. The width of the 405-cm^{-1} line (not shown in Fig. 3) is constant for $T < 150$ K and increases abruptly with temperature for $T > 160$ K.

The temperature dependence of the frequencies of the Raman lines of TaS_3 confirms that it undergoes a phase transition near 220 K.[1] Given the uncertainties in the sample temperatures, it is not possible to extract a critical exponent for this transition from our results. However, they show that the transition is not strongly first order since the shift in phonon frequency near $T < T_c$, which is proportional to the square of the order parameter,[5] is continuous for $T < 220$ K.

The simple mean-field theory for a one-dimensional CDW is quite similar to the theory for superconductivity.[9] The CDW-induced gap $2\Delta(0)$ is related to T_c by the equation $2\Delta(0) = 3.51 T_c$. If we take $T_c = 220$ K, then $2\Delta(0) = 536$ cm^{-1}. Classical linear-response theory[6] shows that the temperature-dependent frequency shift of splitting of a hard mode at a structural phase transition is proportional to η^2. Since $2\Delta(T)$ is proportional to η, we can use Fig. 2 to obtain the dependence of the CDW gap on temperature. This is shown in Fig. 4. Also shown in Fig. 4 are lines representing the nominal energies of the three phonons discussed earlier. At $T = 0$ K, none of the phonons can be damped through the excitation of electron-hole pairs since $2\Delta(0)$ is greater than any of their frequencies. For $T > 60$ K, the 496-cm^{-1} mode can be damped through this mechanism since its energy is now above the gap. The 405- and 283-cm^{-1} lines will show an increase in width due to the excitation of electron-hole pairs for $T > 160$ and 200 K, respectively, i.e., at temperatures where their energies are greater than $2\Delta(T)$. The increases in linewidth will begin at somewhat lower temperatures due to the thermal excitation of carriers across the gap. A comparison of Fig. 4 with Fig. 3 and its discussion shows that this model describes the observed increase of the phonon linewidths.

In addition to the above increase in width, Fig. 3 shows that the width of the 283-cm^{-1} line decreases for $T > 210$ K. A similar effect is observed in the case of our 405-cm^{-1} line. This linewidth variation with temperature can be expected given the formation of a gap at the Fermi surface. The electronic states removed from the vicinity of the Fermi surface by the CDW are to be found near the band edges which define the CDW gap, as in the case of superconductivity,

and there will be an enhancement of the electronic density of states at the band edges. Therefore, the density of states at the Fermi level in the normal state will be smaller than the density of states near the band edges in the CDW state. Since the phonon linewidth contains a contribution proportional to the electronic density of states near the band edges ($T < T_c$) or at E_F ($T > T_c$), the linewidth should show a maximum when the phonon energy is greater than $2\Delta(T)$ and $T < 220$ K.

Sambongi *et al.* also measured the temperature dependence of the resistivity of TaS_3 for $77 < T < 400$ K. They found that the low-temperature resistivity could not be described by an $e^{2\Delta/2kT}$ dependence. Our spectroscopic value for the temperature-induced CDW gap $2\Delta(T)$ provides a reasonably good description of the experimental results of Sambongi *et al.* for $90 < T < 220$ K if we assume that the Fermi level is pinned to the one of the band edges for $T < 220$ K. The number of carriers thermally excited across the gap will then vary as $e^{-2\Delta(T)/kT}$. Measurements[10] of the magnetoresistance of similar compounds such as $TaSe_3$ suggest that the anisotropy of the Fermi surface is not large and that the Fermi surface is quite complicated. It is therefore unlikely that the CDW will completely gap the Fermi surface. This plus the fact that these samples have impurity concentrations in the range 10^{18} to $10^{19}/cm^3$ suggests that the Fermi level could be pinned to one of the band edges.

We have used Raman scattering to study the structural phase transition at 220 K in TaS_3. The temperature dependence of the hard modes shows that the transition is continuous or nearly continuous. We have been able to observe the CDW-induced gap at the Fermi surface for the first time in any CDW system and to measure its temperature dependence. We find that the magnitude of this gap near $T = 0$ is close to that expected on the basis of mean-field theory using the critical temperature of the CDW transition. This result is consistent with those of Monceau *et al.*[11] and Ong[11] in $NbSe_3$ where nonlinear transport data have been interpreted in terms of the creation of a simple mean-field-theory–like gap at E_F. Our results enable us to explain the temperature dependence of the resistivity of TaS_3 in the low-temperature phase. The success of the simple mean-field-theory treatment of the CDW transition in the transition-metal trichalcogenides is in contrast to the failure of such treatments in the transition-metal dichalcogenides where more complicated models involving CDW's with very short coherence lengths have been invoked.[12]

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[a]Permanent address: Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau Cédex, France.

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