Raman Scattering by Superconducting-Gap Excitations and Their Coupling to Charge-Density Waves

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$2H$-$NbSe_2$ undergoes a charge-density-wave (CDW) distortion at 33 K which induces A and E Raman-active phonon modes. These are joined in the superconducting state at 2 K by new A and E Raman modes close in energy to the BCS gap 2Δ. Magnetic fields suppress the intensity of the new modes and enhance that of the CDW-induced modes, thus providing evidence of coupling between the superconducting-gap excitations and the CDW.

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Structural phase transitions involving charge-density waves (CDW) in layered transition-metal dichalcogenides have been studied extensively in the last several years.[1] Neutron diffraction studies[2] on $2H$-$NbSe_2$ show a transition from a normal lattice to one with a three-wave-vector incommensurate CDW at the onset temperature T_d of 33 K. The CDW is only a few percent out of commensurability and the neutron data show that it remains incommensurate down to 5 K. From the modulus measurements of Barmatz, Testardi, and DiSalvo[3] it is concluded that incommensurability persists at least to 1.3 K. $2H$-$NbSe_2$ is a highly anisotropic type-II superconductor below 7.2 K.[4] The upper critical fields at 2 K may be estimated from published data[4] and are found to be 105 and 42 kG for fields parallel and perpendicular to the layers, respectively. Magnetoresistance studies on $2H$-$NbSe_2$ have been carried out by Morris, Coleman, and Bhandari.[5]

Figure 1 shows four pairs of Raman spectra [(a)–(d)] from two different samples of $2H$-$NbSe_2$, M and B, at two different temperatures, 9 K (lower curves in each pair) and 2 K (upper curves) for A and E Raman symmetries. The characteristic CDW-induced amplitude modes (C) are near 40 cm^{-1}.[6] On cooling below 33 K, they first appear, then harden, and get stronger.[7] The main purpose of this paper is to report that when the sample is immersed in superfluid helium at 2 K two new Raman-active modes are seen at 18 cm^{-1} (A) and at 15 cm^{-1} (E), close in energy to the BCS gap at 2Δ. These are labeled G in Fig. 1. It is also noted from this figure that the position of these new peaks (G) is sample independent while the position and strength of the CDW modes (C) are sample dependent. This may be explained by the work of Huntley[8] and Long, Bowen, and Lewis,[9] where it was shown that crystal growth techniques have a small effect on superconductivity whereas Hall-coefficient studies[10] indicate that defects and impurities inhibit the formation of CDW's.

From Figs. 1(c) and 1(d), where all curves have the proper relative intensities, we find that the CDW modes lose intensity when the new "gap" modes appear. This direct coupling between modes C and G is shown more dramatically in

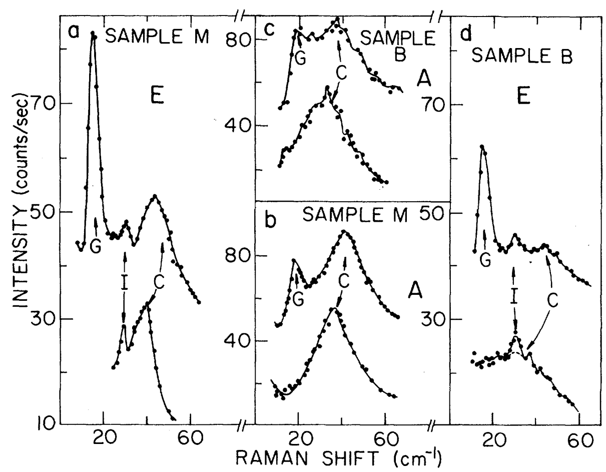

FIG. 1. Raman spectrum of samples M and B. The lower curve of each pair [(a)–(d)] is at 9 K and the upper at 2 K. Raman symmetries [polarizations] are E [(xy)] and A [$(xx)-(xy)$]. C labels CDW modes; G, gap excitations; and I, the interlayer mode characteristic of the $2H$ polytype. Incident laser beam at 5145 Å and 30 mW power was spread into a line 40–50 μm wide. Light was incident at the pseudo Brewster angle; the scattered light collected along the c axis. Resolution was 3 cm^{-1}. Curves (a) and (b) were drawn by hand while (c) and (d) represent a five-point smoothed plot through original data points. The upper curves in the E spectra have been moved up by 20 counts/sec while the A curves in (b) and (c) by 40 counts/sec. The 9- and 2-K data for sample M in (a) and (b) are each from the same run. The same is true for sample B, with the addition that (c) and (d) have been normalized with respect to the intensity of the A_{1g} phonon at about 230 cm^{-1} (Ref. 7).

the presence of a magnetic field. Figure 2 shows the Raman A spectrum of sample B with varying magnetic fields perpendicular to the layers.[11] This spectrum has two features: a CDW-induced mode at about 36 cm^{-1} and the gap peak at 18 cm^{-1}. As H increases, the latter loses strength while the CDW mode is seen to recover. It is difficult to assign any movement to the position of the 18-cm^{-1} mode due to the overlap with the CDW mode. The quantity $\int I(\omega)\omega\, d\omega$ is a constant to within ± 7% for the curves in Fig. 2 when H varies between the values shown. [Here $I(\omega)$ is the number of counts per second at frequency ω after subtracting a common background for all curves.] Thus a sum rule for the total scattering strength seems to hold. Similarly, our data on the E spectrum also show that the new E mode loses intensity rapidly with increasing field while the CDW mode gains strength.

The data in Fig. 2 were obtained with the sample placed at the center of a split superconducting magnet and the Raman signal reflected by a mirror at 45° into the collection optics. Both the magnet and sample were immersed in superfluid helium and the highest attainable field was 42 kG. Because of the smaller window of the magnet coil, the collection solid angle was restricted to about half that in the setup used for Fig. 1. When the sample was superconducting we were able to vary the temperature only between 1.5 and 2 K. No significant changes were noted in this limited temperature range. When the sample was not immersed in superfluid helium, laser heating was sufficient to make it normal.

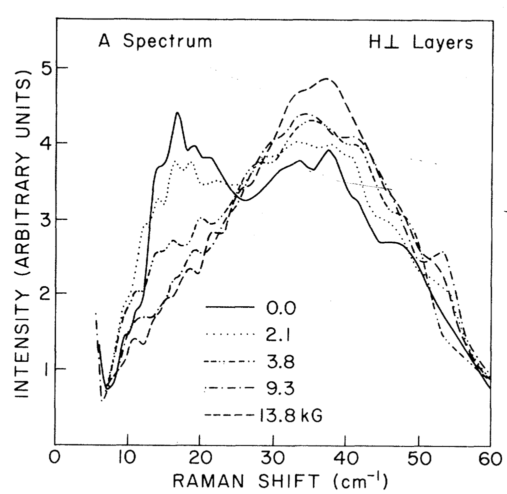

FIG. 2. Raman spectrum with sample immersed in superfluid helium and in the presence of a magnetic field. The resolution was 3 cm^{-1}. The curves represent a five-point smoothed computer plot through the original data points. All curves have been normalized with respect to the intensity of the phonon at about 239 cm^{-1}.

The BCS energy gap at 1.6 K is $2\Delta = 17.2 \pm 0.4$ cm^{-1} as determined by the position of the peak in the infrared transmission.[12] The weighted average of the new Raman peaks is 16 cm^{-1} and essentially agrees with the position of the infrared peak. The gap of any superconductor should in principle be detectable by a Raman-scattering experiment.[13-16] The scattered light at zero temperature is predicted to occur in a continuous distribution with a threshold at 2Δ. However, Raman-scattering experiments to date on superconductors without CDW's, including some of our own preliminary work on Nb, do not reveal the 2Δ gap excitations. These negative results seem to imply weak intrinsic coupling of the light to the gap excitations. McMillan[17] and Balseiro and Falicov[18] have independently suggested that the 2Δ excitations we see in $2H$-$NbSe_2$ borrow their Raman activity from the CDW via electron-phonon coupling. Our field-dependent data clearly show that direct coupling exists between the CDW peaks and the gap peaks. Explicit calculations of Balseiro and Falicov[18] give general agreement with our $H = 0$ results. We note that ω_E, the frequency of the new E mode, is less than ω_A, the frequency of the new A mode. Since the CDW-induced modes themselves differ in frequency, the inequality of ω_E and ω_A might be attributed in part to an unequal renormalization from the electron-phonon coupling. If the coupling were the same for the A and E modes then we would expect ω_A to be less than ω_E. This is contrary to what is observed, implying that the electron-phonon coupling may be symmetry dependent. The difference between ω_A and ω_E may also be attributed to different symmetry-related weighting of the BCS gap over the Fermi surface, thus producing a "bare" Δ_A unequal to a "bare" Δ_E.

In the presence of an applied magnetic field a vortex state exists. The BCS energy gap 2Δ now becomes a spatially dependent quantity, and for high enough fields gapless superconductivity exists. The rapid drop in intensity of the new modes with increasing magnetic field relates to this situation. We do not as yet have a simple picture to describe this effect.

In conclusion, we have seen the 2Δ excitations in a superconductor for the first time, using Raman scattering. This technique has among other advantages good energy resolution and symmetry dependence. This may enable us to obtain information on the anisotropy of the gap from the A- and E-mode splittings. With the aid of theory, the electron-phonon coupling constant may be directly obtained. We may also be able to obtain information on the density of states in the vortex regime when H is large but not close to H_{c2}.

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Phonon Raman Scattering in Superconductors

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If a superconductor has a Raman-active phonon mode of low frequency (larger but of the order of magnitude of the superconducting energy gap 2Δ), we show that electron-phonon coupling leads to a complex bound excitation, also Raman active, with a discrete frequency lower than 2Δ and with intensity which can be appreciable. We propose that these are the lines found by Sooryakumar and Klein at approximately the energy-gap frequency in superconducting $2H$-$NbSe_2$.

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Recent experiments of Sooryakumar and Klein[1] on superconducting $2H$-$NbSe_2$ have detected, in addition to the ordinary Raman lines[2] at 234 and 248 cm^{-1}, and the Raman lines[3] induced by charge-density waves[4-7] (CDW) below $T_{CDW} \cong 33$ K at approximately 40 cm^{-1}, two additional peaks at approximately 16 cm^{-1} which are only present below the superconducting transition temperature $T_{SC} = 7.2$ K. These values seem to agree well with the superconducting energy gap, $2\Delta = 17.2 \pm 0.4$ cm^{-1}, as measured in a different sample by infrared transmission.[8] In addition, these new

