Measurement of the Charge-Density-Wave Gap of $NbSe_3$ from Tunnel-Junction Spectra

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Differential resistance measurements of $NbSe_3$-insulator-lead tunnel junctions as a function of dc bias voltage are reported. The amplitude of the charge-density-wave gap, 2Δ, which occurs in $NbSe_3$ at $T_2 = 59$ K is found equal to 70 ± 5 meV. This value decreases when pressure is applied but the ratio $2\Delta/kT_2 \sim 14$ is pressure independent up to 2.5 kbars. This large magnitude of the charge-density-wave gap, at variance with the BCS value, is interpreted as resulting from the strong-coupling nature of electron-phonon interactions.

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Quasi one-dimensional transition-metal trichalcogenides ($NbSe_3$, TaS_3) and halogenated transition-metal tetrachalcogenides [$(TaSe_4)_2I$, $(NbSe_4)_{10}I_3$] are currently intensively studied because in the charge-density-wave (CDW) state below the Peierls transition temperature, T_P, they exhibit fascinating collective transport properties.[1] The standard description of such a transition comes from the Fröhlich-Peierls mechanism[2] in which some acoustic-phonon mode softens and condenses at T_P leading to a static deformation. The theory, similar to the BCS one for a superconductor, assumes that the gap amplitude, 2Δ, is small compared to the Fermi energy, the so-called weak-coupling limit. However, from measurements of the activation energy in the semiconducting state below T_P,[3] of the infrared bolometric spectra,[4] and of the infrared reflectivity[5,6] in TaS_3 and $(TaSe_4)_2I$, the magnitude of the CDW gap is found to be much larger than the value expected in the weak-coupling limit. One-dimensional fluctuations are known to suppress the transition temperature below the mean-field value.[7] However, $NbSe_3$ is the unique compound among transition-metal trichalcogenides and tetrachalcogenides, maintaining a metallic state at low temperature. Moreover, $NbSe_3$ becomes superconducting when a pressure of 5–6 kbar is applied.[8] Therefore, $NbSe_3$ is often assumed to be less anisotropic than TaS_3 or $(TaSe_4)_2I$ and one-dimensional fluctuations are expected to play a minor role. In this Letter we report on direct measurements of the CDW gap from $NbSe_3$-insulating-lead tunnel junctions. This technique has already yielded values of the CDW gap of the layered compound 1*T*-TaS_2[9] and of the organic compound tetrathiafulvalene-tetracyanoquinodimethane.[10]

$NbSe_3$ crystallizes in a ribbon shape, the broad surface being the (b,c) plane. We have selected $NbSe_3$ single crystals with a width of 150 to 250 μm and with the plane (b,c) as perfect as possible. The native oxidation of the surface was currently sufficient for the insulating barrier. The thickness of the barrier was, however, sometimes increased by heating of $NbSe_3$ samples in the atmosphere at 200 °C for several minutes. The typical size of the junctions was $50 \times 50\ \mu m^2$ and lead was evaporated on the (b,c) plane. Therefore, the tunnel current is perpendicular to this (b,c) plane. A low-frequency current superimposed on the dc bias is applied between one extremity of the crystal and the lead electrode, and the signal detected with a lock-in amplifier; i.e., we measure the differential resistance of the junction in series with the longitudinal resistance of the sample. At room temperature the resistances of the junctions were between 10 Ω and 1 kΩ with a typical value of 100 Ω. Figure 1 shows the variation of the differential resistance dV/dI at zero voltage bias as a function of temperature. The two CDW's appear at $T_1 = 145$ K and $T_2 = 59$ K. Below T_2 the resistance of the junction increases, indicating the opening of the CDW gap. The absence of this rise in resistance reveals a partial short circuit in the barrier and consequently such junctions have been rejected.

We first used a beryllium-copper clamp pressure cell

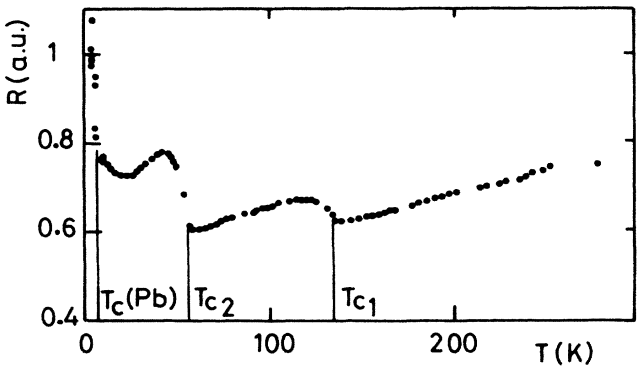

FIG. 1. Temperature dependence of the differential resistance $R = dV/dI$ at zero dc bias of a $NbSe_3$-insulator-lead tunnel junction in series with the longitudinal resistance of the $NbSe_3$ crystal.

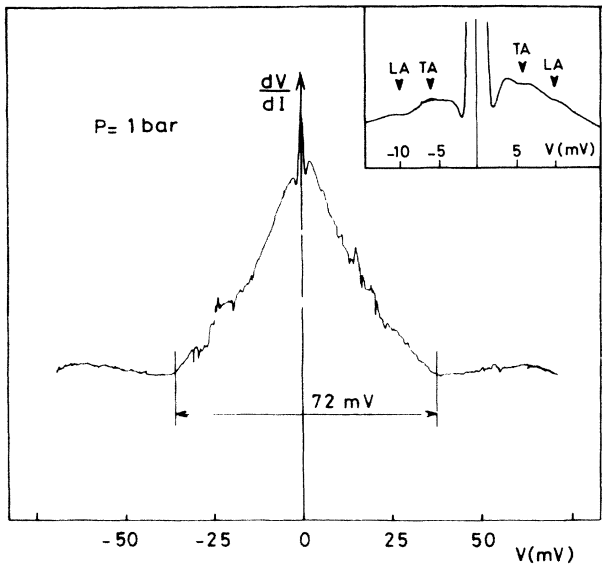

FIG. 2. Variation of the differential resistance dV/dI of a $NbSe_3$-insulator-lead tunnel junction at $T = 1.2$ K as a function of the dc bias voltage. Inset: tunnel spectrum of lead obtained at low voltage.

with a mixture of essence F and oil as the pressure-transmitting medium. We measured a loss of 2.5–3 kbar at the solidification of the liquid. Tunnel junctions are very sensitive to pressure, mainly to nonhydrostatic stresses which are inherent to the clamp technique and also because of the extrusion of lead through the barrier. We tried to prevent this last effect by using a lead–2%-indium alloy as an electrode, without a definite improvement. We have not been able to avoid short circuits in the junctions when the applied pressure exceeded 3–4 kbar at room temperature and consequently no significant pressure was retained at low temperature.[11] Therefore, we have used a piston-cylinder apparatus in which pressure is generated at 4.2 K or below by direct compression of liquid and solid helium.[12] At a fixed temperature in the helium temperature range, pressure can be continuously changed from 1 bar to several kilobars. With such a system, nonhydrostatic stresses are much smaller than in the clamp technique and no temperature cycling is necessary to modify pressure; consequently, tunnel junctions have been kept working up to 2.5 kbars. The pressure has been measured with a In-Sb calibrated manometer.

Figure 2 shows the variation of the differential resistance dV/dI of the junction as a function of the voltage bias at ambient pressure and $T = 1.2$ K. The spectrum of lead obtained at low voltage bias is drawn in the inset with an enlarged scale. It is well known that for a superconducting-insulator-metal junction dI/dV is directly proportional to the density of states $N(E)$ at the Fermi level which, in the BCS theory, diverges at $\pm\Delta$. Therefore the superconducting gap of lead is measured when dV/dI sharply increases; its magnitude is 3.2 meV. The characteristic sideband anomalies at 5 and 9 meV which are the phonon energies for bulk lead are also clearly identified.[13] In $NbSe_3$ the CDW condensation below $T_2 = 59$ K does not affect the whole Fermi surface. Consequently the density of states is only weakened below T_2 which leads to a broad variation of dV/dI as a function of the voltage bias with a shape similar to that induced by zero-bias anomalies. However, it is commonly recognized that the observation of the lead structure is proof of a good tunnel junction.[14] The gap, 2Δ, for the lower CDW transition ($T_2 = 59$ K) is measured between the voltage values where dV/dI shows a discontinuity. We obtain $2\Delta = 72$ meV. From measurements on several junctions we estimate that at ambient pressure $2\Delta(T=0) = 70 \pm 5$ meV and consequently $2\Delta(T=0)/kT_2 = 13$–14 meV. A much smaller value of the gap ($2\Delta/kT_2 \sim 3.5$) has been, however, derived from far-infrared reflectance performed on a collection of loosely assembled parallel fibers but with a random transverse orientation.[15]

Tunnel spectra as a function of pressure at $T = 1.8$ K are shown in Fig. 3. It is seen that singularities in dV/dI are less pronounced and therefore the measurement of 2Δ is less accurate. The variation of 2Δ as a function of pressure is drawn in Fig. 4. We deduce that the CDW gap decreases linearly with pressure with a slope of -12 meV/kbar. By resistivity measurements under pressure it has been previously shown that T_2 also decreases with pressure linearly up to 4 kbar with a slope of $dT_2/dP = -6.25$ K/kbar.[8] Consequently $2\Delta/kT_2 = 13$–14 is pressure independent up to 2.5 kbar.

Two features in the tunnel spectra have to be noted. For voltages beyond ± 35 mV the variation of dV/dI is

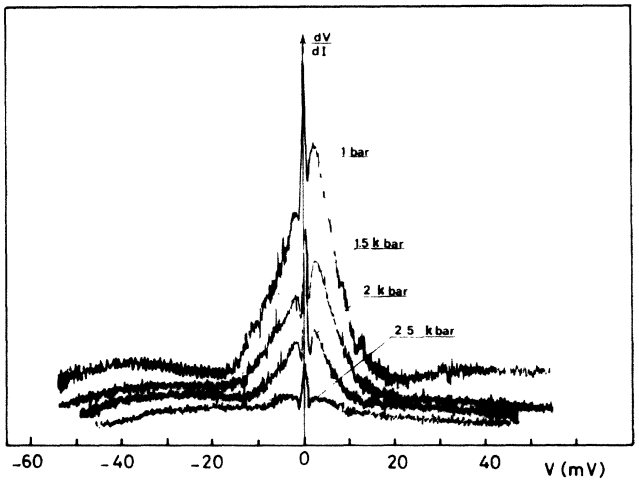

FIG. 3. Variation of the differential resistance dV/dI of a $NbSe_3$-insulator-lead tunnel junction at $T = 1.8$ K as a function of the dc bias voltage at several pressures.

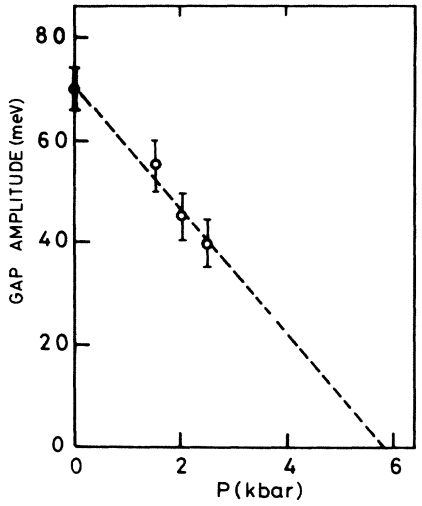

FIG. 4. Variation of the gap amplitude (at $T = 1.8$ K) of the lower CDW transition of $NbSe_3$ ($T_2 = 59$ K) measured from tunnel spectra of Fig. 3 as a function of pressure.

not flat, which may indicate a tunnel process related to the upper CDW ($T_1 = 145$ K). However, measurement of such a gap cannot be achieved because of heating problems in the sample. Secondly, spectra show a maximum at $V \neq 0$ at ambient pressure, but this asymmetry disappears when P is increased. This offset is often related to the asymmetry of the barrier consecutive to a difference in barrier height.[14] This possibility is likely because we have used single crystals which may have steps on the surface and we have not controlled the oxide layer.

The conventional mean-field theory for the Peierls transition assumes a weak interaction between electrons and the classical deformation field and ignores fluctuations.[2] Within these conditions the CDW gap is found equal to ~ 3.5 times the mean-field transition temperature and the major contribution ot the entropy at the phase transition comes from electronic excitations through the gap. Large values of $2\Delta/kT_P$ require that the measured transition temperature be reduced below the mean-field value. This reduction has been tentatively explained in two different ways. First, in the absence of interchain coupling one-dimensional fluctuations shift the phase transition to 0 K. T_P has been shown to depend on the strength of the three-dimensional coupling between chains[16] by a relation similar to that for the superconducting transition temperature in the McMillan theory of strong-coupling superconductors. On the other hand, McMillan has proposed a model of the CDW transition with a strong electron-phonon coupling.[17] In this model the coherence length is very short, of the order of magnitude of the superlattice unit cell, and the phonon frequencies are softened over a large region of the reciprocal space near the CDW wave vector. Therefore, the phonon entropy is very large at the phase transition and dominates the electronic entropy. A microscopic theory of the same model with anharmonic interaction among phonons induced by electron scattering has been recently developed by Varma and Simons.[18] This short-coherence-length model describes fairly well the properties of layered compounds such as $2H$-$TaSe_2$ or $2H$-TaS_2. In these compounds $2\Delta/kT_P \sim 24$[19] and the jump in specific heat at T_P is ~ 5–7 times[20] the value expected from the weak-coupling BCS theory. Recently, phonon thermal conductivity has been measured to be ~ 3–4 times larger than the electronic thermal conductivity estimated from resistivity on the assumption of the Wiedemann-Franz law.[21] Following McMillan, the phase transition does not then result from the softening of an acoustic mode but can be seen as an order-disorder transition: Above T_P, localized CDW modes with localized electronic energy gap in each superlattice cell form a polaron liquid which condenses at T_P establishing long-range-order phase coherence below T_P. In a similar context Le Daeron and Aubry have studied the ground state of a Peierls chain as a function of the electron-phonon coupling. They showed that above a critical value the lattice periodic distortion and the CDW cannot be described by a periodic function but by a nonanalytic and discontinuous function[22] (the so-called "transition by breaking of analyticity").

One-dimensional fluctuations are currently detected by precursor effects above T_P, such as, for instance, for TaS_3 or $(TaSe_4)_2I$, diffuse lines in diffuse x-ray or electronic diffraction measurements,[23] or fluctuative contributions to the electrical conductivity.[3] However,

$NbSe_3$ is not extremely anisotropic [a ratio of ~ 30 in conductivity in the plane (b,c) and around 100–200 perpendicular to (b,c)] which makes this compound similar to two-dimensional layered compounds. Observation of diffuse lines has, however, been reported[24] but the original of this diffuseness is questionable and may result from the interaction of the CDW with impurities. Calorimetric measurements near T_1 and T_2 do not seem to reveal large changes in entropy.[25] However, thermal conductivity measurements show that the phonon thermal conductivity is ~ 4–7 times the electronic thermal conductivity[26] and rises smoothly below T_2 (when the electronic contribution decreases because of the loss of carriers) in exact similarity with the measurements on $2H$-$TaSe_2$ (compare Fig. 4 in Ref. 26 to Fig. 2 in Ref. 21).

From $NbSe_3$-insulator-lead tunnel-junction spectra we have measured the CDW gap amplitude, 2Δ, of the lower CDW in $NbSe_3$ ($T_2 = 59$ K); $2\Delta/kT_2 \sim 13$–14 and is independent of pressure up to 2.5 kbar. We have pointed out that this result (as thermal conductivity) makes $NbSe_3$ very similar to layered compounds such as $2H$-$TaSe_2$ and we relate the large CDW amplitude to the strong-coupling nature of electron-phonon interactions in $NbSe_3$. It is expected that unambiguous correlation lengths will be deduced from phonon dispersion measurements actually in progress.[27] The strong electron-phonon interaction revealed in this present experiment may modify the current description of the CDW dynamics which are intensively studied in $NbSe_3$ as well as in related compounds.

We would like to thank F. Levy for providing us with many broad $NbSe_3$ crystals.

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