Electron Tunneling Study in the $NbSe_3$ Charge Density Wave State

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A study using tunneling spectroscopy of the density of states in the vicinity of Fermi level has been performed on $NbSe_3$ at low temperature. The tunneling conductance data reveal an asymmetry with respect to the Fermi level and below 4.2 K two minima. These results definitely establish the semimetallic character of $NbSe_3$ at low temperature. Tunneling spectra have been analyzed assuming an anisotropic gap structure, and the transverse coupling energy derived is in good agreement with band calculations.

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It is now well known [1] that broken-symmetry ground states arise in quasi-one-dimensional (Q1D) systems as a consequence of electron-phonon interactions. This ground state, called a charge density wave (CDW), formed by a periodic lattice modulation and a concomitant charge modulation develops below the Peierls transitions temperature T_p. Below T_p a gap appears in the single particle excitation spectrum with an amplitude defined at zero temperature in the mean field approximation by the BCS expression $2\Delta(0) = 3.5kT_p$.

One of the main difficulties in the physics of Q1D materials is the estimation of the interchain coupling. If the system is really 1D, large fluctuations are expected and the Peierls transition temperature is strongly reduced below the mean field transition temperature [2]. Fluctuation effects may account for the large $2\Delta(0)/kT_p$ ratio, typically in the range of 8–12, measured in such systems [1]. But a finite transverse coupling induces a wrapping of the bands which may overlap and consequently yields a semimetallic state. As reported hereafter we have been able in the case of $NbSe_3$ by tunneling spectroscopy to estimate this transverse coupling energy ε_0, and we have found that it is larger than the CDW gap. This result allows us to reinterpret previous tunneling spectroscopy data [3,4]: The singularities in the density of states do not appear at $\pm\Delta_0$ but at $\pm(\Delta_0 + \varepsilon_0)$. Hence we can reconcile the values of the gap amplitude deduced from far infrared measurements [5] and those obtained by tunnelings.

$NbSe_3$ exhibits two independent Peierls transitions at $T_{p1} = 144$ K and $T_{p2} = 59$ K with incommensurate wave vectors. Band structure calculations [6–8] tend to demonstrate that the first CDW transition corresponds to a nearly perfect nesting between two quasiparallel sheets of the Fermi surface (FS), while the second transition is due to an imperfect nesting of the remaining FS. So electron and hole ellipsoidal pockets exist at the FS at low temperature as revealed by large Shubnikov–de Haas oscillations in the magnetoresistance [9,10].

In principle, tunneling spectroscopy [11] is a specific technique for deriving the consequence of the Peierls transition on the density of states. Surprisingly, publications concerning this technique applied to Q1D conductors are rare [3,4]. The spectroscopy technique that we have used is a classical "planar junction technique." Dots of lead (2000 Å thick) are evaporated on the (*b*,*c*) surface of $NbSe_3$ crystal in a vacuum group through mylar masks. The tunneling data are collected using a phase-sensitive detection, which allows an analogic measurement of the differential tunneling resistance by the classical four probe technique. Because of the shape of the crystals, we have only been able to realize junctions on the (*b*,*c*) plane.

In the use of a superconducting lead counterelectrode is essential to verify the quality of the insulating layer. It has been demonstrated [12] that in the case of a metal-insulator-superconductor junction the tunneling conductance is proportional to the superconducting density of states. So it is possible to verify the quality of the junctions by the observation of the lead superconducting phase (gap and phonons) and the exact position of Fermi level.

In the use of the WKB approximation only the component (normal to the junction plane) of the wave vector associated with the electron which tunnels needs to be taken into account. We can deduce that the tunneling spectroscopy samples the density of states (DOS) in a crystallographic direction normal to the junction plane; hereafter this will be noted "DOS."

A study of the DOS of $NbSe_3$ by tunneling spectroscopy and its modification under pressure has clearly shown [3]

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a partial condensation (75%) of the DOS between the high and low temperature phases. The pressure dependence of the DOS was in agreement with the transport measurements showing the total suppression of the CDW gap, at approximately 6 kbar. However, because of the structures associated with the superconducting lead, evolution of the DOS around the Fermi level below T_{p2} was not revealed. Indeed, when lead is in the normal state (by application of a magnetic field), a progressive energy offset of the DOS minimum appears when T decreases, and in good junctions below 4.2 K, two minima in the DOS can be seen on either side of the Fermi level. Following previous work [13] on η Mo_4O_{11}, we will attempt now to correlate these phenomena with a simple band scheme.

A typical tunneling conductance curve of a $Pb/I/NbSe_3$ junction at $T = 1.2$ K is shown in the upper part of Fig. 1. The energy gap and phonons from the Pb are clearly visible. After having suppressed the lead superconducting phase by applying a 3 kG magnetic field, we can see the $NbSe_3$ DOS at 1.2 K. The positive side of the bias voltage in the differential conductance corresponds to the conduction band of $NbSe_3$, whereas the negative side corresponds to the valence band. Two minima located on either side of the Fermi level exist. The first minimum is situated at 1.5 meV in the conduction band, and the second is at 1 meV in the valence band. The Fermi level corresponds to a relative maximum of the DOS.

In the lower part of Fig. 1 the evolution of the previous DOS magnified by a factor 5 at 1.2, 4.2, and 7 K is represented. It can be seen that the two minima quickly disappear when the temperature is raised. Above 7 K there is only one minimum which is situated in the conduction band. The relative maximum of the DOS at the Fermi level has completely disappeared.

The evolution of the differential tunneling resistance as a function of the bias voltage at given temperatures is shown in Fig. 2. The offset of the maximum of the resistance appears clearly when the temperature is reduced below T_{p2}.

Many authors [9,14] have shown that experimental results such as Hall resistance, Shubnikov–de Haas oscillations, and the conduction in the Ohmic regime could be explained by means of a simple scheme of two parabolic bands, a conduction and a valence band. This has been theoretically [6] demonstrated by calculating the dispersion relationships taking into account the nonequivalent character of each $NbSe_3$ chain in the unit cell.

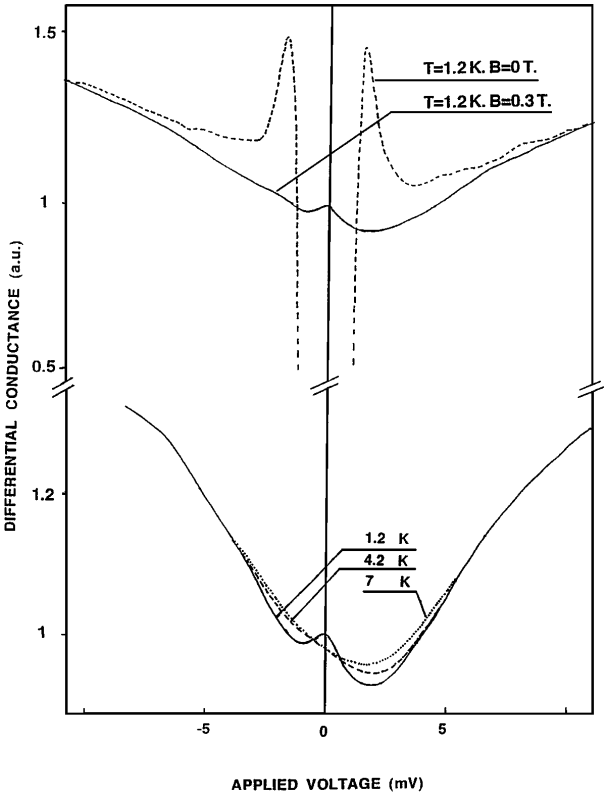

FIG. 1. Upper part, the dashed line represents the tunneling conductance $Pb/I/NbSe_3$ junction at 1.2 K. The full line represents the $NbSe_3$ DOS along the a axis at 1.2 K with a 0.3 T magnetic field to suppress the lead superconductivity. In the lower part the magnified evolution of the DOS versus bias voltage for different temperatures is represented.

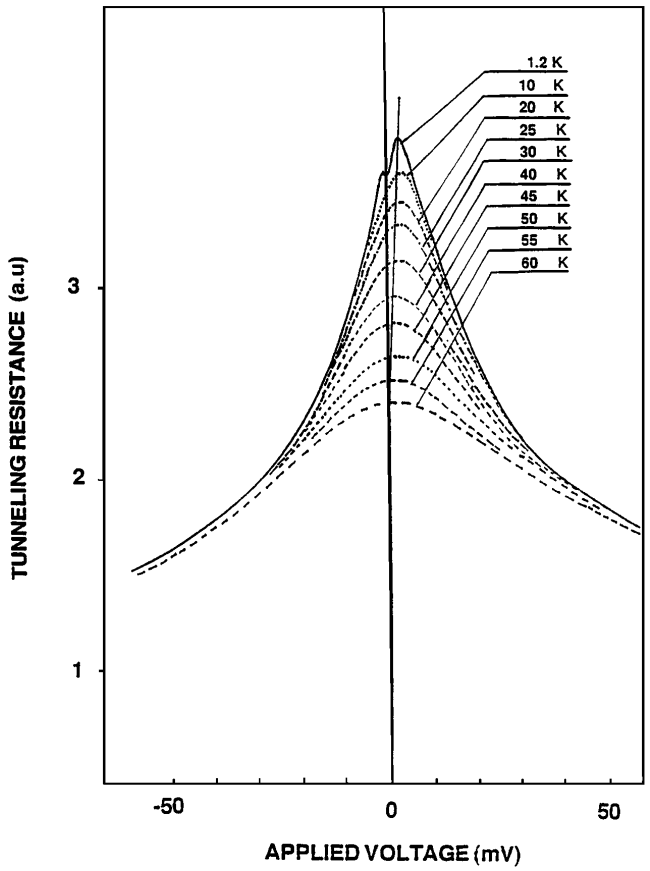

FIG. 2. Evolution of the differential tunneling resistance associated with the DOS versus bias voltage for temperatures lower than the second CDW transition temperature. The progressive offset of the maximum of the resistance appears clearly.

According to Esaki [11], we can correlate the DOS experimentally found at 1.2 K (Fig. 2) with that deduced from to a two-band scheme, a valence and a conduction band overlapping near the Fermi level. The relative maximum of the DOS at null bias voltage is due to a maximum overlapping between these bands at E_F. The two minima in the DOS correspond to the band edges. We can deduce that the conduction band edge is situated at 1 meV below the Fermi level, and the valence band edge is situated at 1.5 meV above the Fermi level. However, imperfect nesting due to coupling between chains should be taken into account. As theoretically calculated by Yamaji [15], the transverse transfer energy ε_0 modulates the valence and the conduction bands in the reciprocal space perpendicularly to the nesting direction. A schematic band scheme at low temperatures is drawn in Fig. 3(a) ε_0 is defined as

$$\varepsilon_0 = t_{a^*}^2 \cos(bk_f)/2t_b \sin^2(bk_f)\,.$$

t_{b,a^*} are, respectively, the coupling energy along the nesting direction and along a direction perpendicular to it. It is easily seen from Fig. 3(a) that if $\varepsilon_0 < \Delta$, where Δ is the mean field gap amplitude, the compound is semiconducting with an apparent gap amplitude $2(\varepsilon_0 - \Delta)$, while if $\varepsilon_0 > \Delta$ this compound is a semimetal due to the band overlap. In this latter case it has been shown by Huang and Maki [16] that the DOS exhibits symmetrical minima with respect to the Fermi level at energy $\varepsilon_0 - \Delta$. In the frame of this two-dimensional theory and assuming the gap of the lower CDW to be BCS type as found in far-infrared spectroscopy measurements [5], ε_0 is estimated at 10 meV. This value is in good agreement with that derived from dispersion relationships [8] and from the anisotropy observed in the electric conductivity [17]: $t_b/t_{a^*} = 5$ and $t_b = 0.275$ eV, which gives $\varepsilon_0 = 8$ eV.

However, an asymmetry in the DOS spectra between the conduction and the valence bands is experimentally found. This asymmetry might be due to the finite interchain coupling in the third direction along the c axis [16].

With these results, one may calculate the tunneling conductance. For simplicity, we have made the hypothesis that near the extrema the valence and conduction bands could be modelized as parabolic bands $N_e(E) \propto E^{1/2}$ and $N_h(E) \propto 1.1E^{1/2}$ as represented in Fig. 3(b), with a ratio $N_h/N_e = 1.1$ estimated by Coleman *et al.* [9].

The differential tunneling conductance is calculated from the expression derived by Cohen *et al.* [18].

$$\frac{dI}{dV}(V) \propto \int N(E)\,\frac{1}{kT}\,\frac{\exp[(E - eV)/kT]}{\{1 + \exp[(E - eV)/kT]\}^2}\,dE\,, \tag{1}$$

where $N(E)$ represents the DOS associated with the CDW phase for an energy E at a temperature T. With the rigid band model of Fig. 3(b), the differential conductance curves computed according to Eq. (1) are shown in Fig. 4(a) at given temperatures. The curves show a crossing at an energy of the order of 8 meV which has not been observed experimentally. We have therefore assumed that there is a band splitting which increases when T is reduced below T_{p2} and that the extrema of the bands follow the mean field law according to the Peierls theory. The extrema of the two bands evolve according to the following expressions:

$$\begin{aligned} E_{\text{val}}^{\max} &= \Delta_0[1 - (1 - T/T_p)^{1/2}] + \Delta_{\text{cross}}\,, \\ E_{\text{con}}^{\min} &= -\Delta_0[1 - (1 - T/T_p)^{1/2}] - \Delta'_{\text{cross}}\,. \end{aligned} \tag{2}$$

Δ_{cross} and Δ'_{cross} are the values of the overlapping bands at 1.2 K taken from the Fermi level (respectively, 1.5 and 1 meV) and Δ_0 the maximum value of the

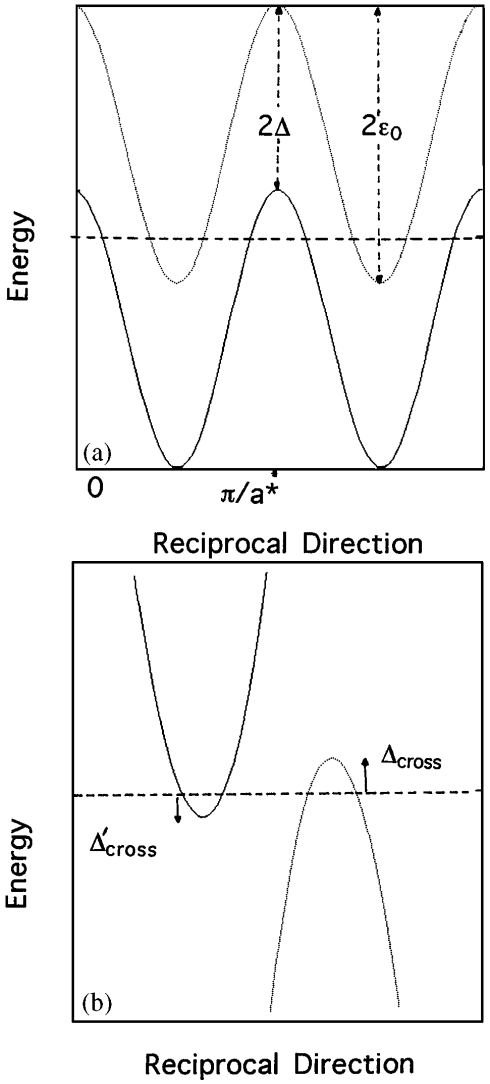

FIG. 3. (a) Band scheme representation of the dispersion relationships along the a^* direction, in the framework of the Yamaji model [15]. We have supposed that $\varepsilon_0 > \Delta$, so the compound is semimetallic. (b) The parabolic band scheme used for the numerical simulations. The horizontal dashed line represents the Fermi level.

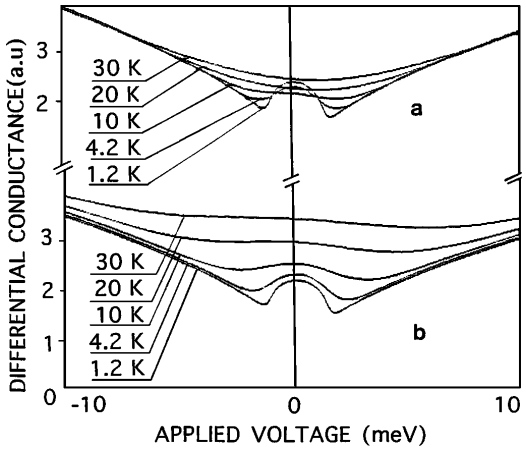

FIG. 4. Computed simulation of the differential tunneling conductance for various temperatures deduced from the previous band scheme with different values of Δ_0. The minimum of the valence band is taken at 1 meV below the Fermi level, and the maximum of the conduction band is situated at 1.5 meV above the Fermi level. (a) We have taken $\Delta_0 = 0$ meV corresponding to a static model. (b) $\Delta_0 = 8.9$ meV which corresponds to the mean field model.

band overlap between 1.2 K, and T_{p2} as in the mean field approximation $2\Delta_0 = 3.5kT_{p2}$. Within this last model the differential tunneling conductance is shown in Fig. 4(b). The difference between the experimental data and the computed curves may result from the parabolic shape of the bands that we have used.

On the basis of the different experimental and simulated results, we can deduce that the evolution of the DOS in $NbSe_3$ along the a^* axis, for temperatures below the second transition temperature, may be modelized by a two-band scheme, a valence and a conduction band, which split when T is lowered. An overlap between these bands at 1.2 K, corresponding to the electron and hole pockets at the Fermi surface, results. The minimum of the conduction band is situated at 1 meV below the Fermi level, and the maximum of the valence band is situated at 1.5 meV above the Fermi level.

Using the model developed by Yamaji [15], we have determined the transverse coupling energy along a^* to be about 10 meV. This energy is larger than the mean field CDW gap and is in good agreement with band calculations. Consequently, the singularities which, in the strict one-dimensional case, should appear at $\pm\Delta(0)$ are masked due to the large transverse coupling between chains in $NbSe_3$. In the two-dimensional case (Yamaji model), Huang and Maki [16] established that the DOS is affected by the CDW transition on a domain larger than $\varepsilon_0 + \Delta(0)$ on either side of the Fermi level. This value, by taking a BCS gap value and a transverse coupling energy around 10 meV, is 20 meV and is of the same order of magnitude as the experimental value measured in previous tunneling experiments [3,4].

Finally, our tunneling data clearly show that at low temperatures the ground state of $NbSe_3$ is semimetallic, as in bismuth. The analysis that we have made is quite general and may be used for several Q1D systems in the study of the interplay between the gap amplitude and the transverse corrugation of the Fermi surface due to imperfect nesting. In fact, Yamaji first proposed his model to describe a semimetallic state in the spin density wave organic compound $(TMTSF)_2PF_6$.

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