Charge Density Wave Gap Formation of $NbSe_3$ Detected by Electron Tunneling

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Tunneling spectra of $NbSe_3$ between 77 K and room temperature have been measured carefully. A charge density wave (CDW) pseudogap exists up to a temperature higher than ~260 K. While the gap parameter undergoes an accelerated change between ~130 and ~160 K, the junction conductance at zero bias does not show any anomaly around $T_1 = 145$ K, the upper CDW transition temperature. Below the mean field transition temperature there are four regimes: a regime where a true CDW state exists, a regime where pinned and mobile CDW coexist, a regime of a pseudogap, and a regime where the CDW fluctuation can barely be detected by current measurements. [S0031-9007(98)08284-2]

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Since the discovery of the non-Ohmic conductivity in $NbSe_3$ about 20 years ago [1,2], colorful phenomena have been observed in the material and other inorganic quasi-one-dimensional (Q1D) compounds, which can be well described by a sliding charge density wave (CDW) [3]. Comparatively, not so much attention has been paid to the behaviors at and above the CDW transition where strong phase fluctuations are expected because of the Q1D nature of the materials. For example, $NbSe_3$ undergoes two CDW transitions at $T_1 = 145$ K and $T_2 = 59$ K, separately. While it is generally believed that the Fermi surface (FS) nesting is perfect for the T_1 transition, the estimations of the FS annihilation at the transition are scattered by different measurements. Using the resistivity anomaly, Ong and Monceau [2] estimated a FS loss of ~20% at T_1, as compared to a 60% loss at T_2. Specific heat data lead to about the same value of FS annihilation at T_1 and T_2 [4]. In contrast, a susceptibility measurement agreed with a FS loss at T_2 only less than one-half of that at T_1, and the annihilation process spread over quite a wide temperature range below T_1 [5]. However, all these estimations were obtained from indirect measurements. It would be interesting by tunneling experiment to get direct information about how the CDW gap and the density of states (DOS) of electrons at the FS change through the CDW transition. The experiment can also give further information about phase fluctuation above the transition. Sorbier *et al.* [6] made a detailed tunneling study in $NbSe_3$ for temperature below 60 K. The present Letter reports detailed measurements of the tunneling spectroscopy of $NbSe_3$ from 77 to 300 K, putting stress on the gap formation at T_1.

Two kinds of junctions were made for the measurements. In one kind of junction, the $NbSe_3$ crystal was laid on a sapphire substrate with the (b, c) plane parallel to the substrate surface. A thin (20 μm in diameter) Nb wire was put across the sample and gently stretched to apply a tiny force at the contact. In this way we could often make stable tunnel junctions whose energy barriers were formed by the oxide layers of the crystals. In an alternative version a thin strip of tin film perpendicular to the chain was deposited on the (b, c) surface of the $NbSe_3$ sample, making an $\sim 20 \times 20\ \mu m^2$ $NbSe_3$-insulator-tin junction area. The junction resistances ranged from 100 to 10 kΩ for the measured samples. The differential tunneling conductance dI/dV was measured by slowly sweeping the dc bias modulated by a small ac signal (~321.8 Hz, 1–3 mV). dI and dV were picked up, separately, by two lock-in amplifiers.

Typical tunneling spectra for a $NbSe_3$-I-tin junction at different temperatures are shown in Fig. 1. We see clearly the development of the CDW gap with the decrease of temperature. To get some quantitative results of the process, two things have to be made. First, we need to determine when the gap begins to appear. We believe that within the resolution of our measurement, this happened around 260 K because all the dI/dV vs V curves above the temperature were very similar and could be approximately described by parabolas whose vertices slightly shifted from zero bias. This means that the energy barrier was almost symmetrical and in this temperature range the gap, if any, became indistinguishable. The second thing is to clarify the temperature modifications since we are measuring tunneling spectra at relatively high

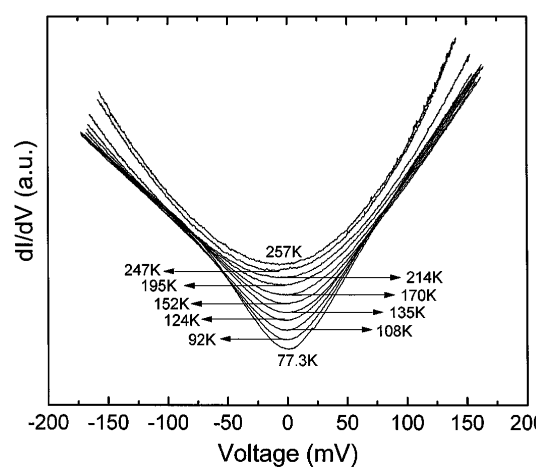

FIG. 1. Tunneling spectrum for a $NbSe_3$-I-tin junction measured between 77 and 260 K.

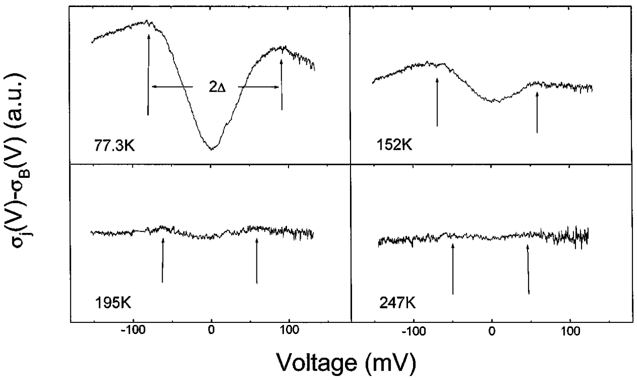

FIG. 2. The same data as in Fig. 1 after subtracting a parabolic background for selected temperatures. The existence of a pseudogap of 247 K can clearly be seen from the figure.

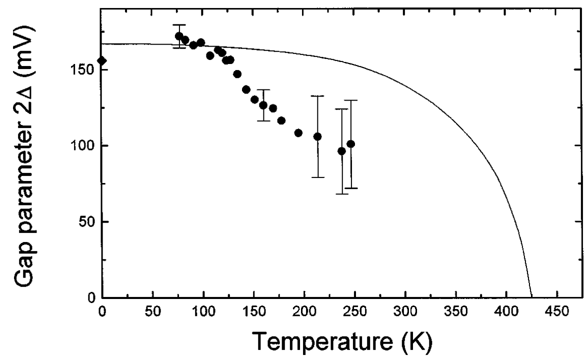

FIG. 3. The obtained gap $2\Delta(T)$ at different temperatures (circle). Data at 1.2 K (diamond) are taken from [9]. The solid line gives a BCS-like temperature dependence of the gap with $2\Delta(0) \sim 4.5kT_p$.

temperature. Engler [7] shows a general formula for the correction

$$N(V) = \sigma_j(V) - \frac{(\pi kT)^2}{3!e^2}\frac{d^2\sigma_j}{dV^2} + \cdots, \qquad (1)$$

where $N(V)$ is the DOS and σ_j is a normalized differential junction conductance. By fitting our data with Eq. (1), we find, fortunately, that the temperature modification was not a serious problem. The corrections were usually less than 3% [8]. After making the temperature corrections and subtracting the parabolic background of the DOS, we obtain the change of the DOS associated with the CDW gap development (see Fig. 2). The temperature dependence of the gap parameter 2Δ thus obtained is shown in Fig. 3, which were similar for all the measured junctions, though the absolute values of 2Δ were somewhat sample dependent. The data obtained here are also consistent with our recent measurements at low temperatures where $2\Delta \sim 156$ meV were observed at 1.2 K [9]. For comparison, in Fig. 3 we have plotted a BCS-like T dependence of 2Δ with (arbitrarily) $2\Delta(0) \sim 4.5kT_p$. T_p is the mean field transition temperature when there were no fluctuations. This choice of T_p does not affect the conclusion of the following discussion. Several features immediately emerge from the figure. First, we see that 2Δ roughly follows the BCS curve below ~100–130 K above which the decrease of 2Δ is accelerated until around 160 K. Second, the gap parameter continuously passes the upper CDW transition and extends to a temperature as high as ~260 K. To our knowledge, this is the first experiment which proves the existence of a pseudogap above T_1 for $NbSe_3$. Johnston *et al.* have shown that susceptibility data of some Q1D materials indicate that a pseudogap could exist well above their Peierls transition temperatures [10]. Third, the pseudogap becomes indistinguishable at a temperature where 2Δ does not vanish.

An interesting issue, related to the gap development, is how the DOS at the Fermi energy, $N(E_F)$, changes around T_1. For a phase transition of first order, one expects some jump of $N(E_F)$ at T_1, while for a second order transition, a kink in $N(E_F)$ vs T plot, or a jump in $dN(E_F)/dT$ vs T plot, at T_1 should be observed. Many properties, for example, the Hall coefficient [11], thermopower [12], and magnetic susceptibility [4], show a kind of kink at T_1. However, for a material with complicated Fermi surfaces and many striking features, some of which are still not well understood, the relations of these quantities with $N(E_F)$ are not straightforward. Since Fig. 3 seems to lack a drastic change in 2Δ at the vicinity of T_1, we decided to trace the temperature dependence of the junction conductance in detail at zero bias, $\sigma_j(0)$, which should have a one-to-one correspondence to $N(E_F)$. The result is shown in Fig. 4. To check whether the curve does reflect the change in $N(E_F)$, we have also traced the change of $\sigma_j(V)$ with T at high bias ($V = 110$ mV), beyond the gap region. In the latter case $\sigma_j(V)$ is essentially independent of T. This means that the junction barrier of this sample was very stable in the thermal cycle. The weak T dependence of σ_j (110 mV) is approximately consistent with the temperature modification of Eq. (1). Since, as we mentioned earlier, the temperature modification in Eq. (1) is not a serious problem in our case, the change of $\sigma_j(0)$ is indeed caused by the change of $N(E_F)$.

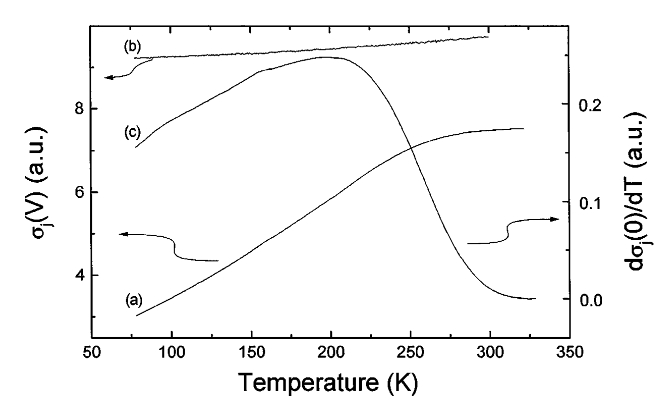

FIG. 4. The temperature dependence of the junction conductance $\sigma_j(V)$ at (a) zero bias, (b) at $V = 110$ mV, and (c) the derivative of $\sigma_j(0)$ with temperature.

The 2Δ and $\sigma_j(0)$ so obtained are not independent. We expect that while $\sigma_j(0)$ decreases with lowering temperature, meaning that more electrons are condensed into the CDW, 2Δ should increase. This is confirmed from the results of Figs. 3 and 4. However, a simple scaling relation does not exist between the two quantities. First, a rapid increase in $\sigma_j(0)$ between $\sim$130 and $\sim$160 K corresponding to the structures of $\Delta(T)$ in the same temperature range was not found. Second, $\sigma_j(0)$ increases continuously to a saturated value where the pseudogap still has a definite width. The lack of simple relation between 2Δ and $\sigma_j(0)$ is quite natural because, while $\Delta(T)$ depends on the characteristic coherence length of the fluctuated CDW clusters at a given temperature, $\sigma_j(0)$ depends on many factors: the size, the number, and, maybe more importantly at high temperatures, the lifetime of the CDW clusters. Although thermal energy affects the formation and lifetime of the CDW clusters consistently, the lack of synchronous changes of these two parameters may imply that some other factors, e.g., the interface energy between the CDW clusters and the background normal phase, must be taken into account.

It was very surprising that we could not detect any anomaly in the junction conductance at zero bias at T_1. Several junctions were measured in repeated thermal cycles to check the phenomenon, and it was found that the smooth change of $\sigma_j(0)$ was reproducible. The result raises at least two important issues which need to be considered seriously. The first issue is how to reconcile the present finding with many previous observations, such as specific heat, resistivity, Hall effect, etc., all of which clearly show anomalies at T_1. The second issue is, whereas the CDW condensation continuously extends to far above T_1, why it does not manifest itself in transport measurements. At present, we do not have enough knowledge to give a definite answer to the two problems, but the picture described in the following could be a reasonable explanation.

In regard to the first issue, we notice that although $N(E_F)$ continuously passes through T_1, 2Δ undergoes a rapid rise below $\sim$160 K. This is usually ascribed to the crossover from the one-dimensional fluctuation regime to a true three-dimensional ordered phase. That is, the interchain coupling below T_1 surpasses the thermal energy. Two factors may contribute to the anomaly at T_1. First, the mobile, fluctuated CDW clusters rapidly combine into larger ones, not necessarily accompanied by a rapid change of total condensed electrons. Second, a true equilibrium between the condensed electrons and the lattice distortion is realized below T_1; above $\sim T_1$, the heavy lattice cannot follow the rapid temporary changes of the electron system, and, hence, the corresponding superlattice could be much weaker than a true thermodynamic equilibrium needs. The weak coupling between the CDW clusters and the lattice also means the absence of a pinning force. True equilibrium between the electron and lattice systems is realized only by cooling the sample below T_1 where the change in lattice distortion may be more drastic than in electronic structure, giving rise to strong pinning of the CDW by the lattice and resulting in various transport anomalies at T_1.

To answer the second issue of why the pseudogap does not influence the transport above T_1, we find it is not really a new puzzle unique to the fluctuation regime. It has been known for a long time that for the inorganic Q1D conductors in their CDW state, the conductivity is just the same as if the CDW condensation did not exist once the CDW is completely depinned. This feature was well demonstrated for $NbSe_3$ [1] and the phenomenon has not been well understood up to now. Since in the fluctuation regime the CDW clusters are very mobile, which is supported from the lack of the depinning threshold field above T_1, it is, therefore, not surprising that the transport properties behave as if there were no CDW fluctuation. The tunneling spectra are insensitive to the dynamic behavior of the CDW clusters. This point of view was tested in our experiment by recording simultaneously the tunneling spectra and the sample differential resistance below T_1. While a clear threshold appeared in the latter, there was not any difference in the tunneling spectra before and after the CDW began to slide.

If the above discussion is reasonable, one should be careful when trying to deduce the Fermi surface loss at T_1 by transport measurements or by specific heat anomaly. The specific heat anomaly may essentially contribute to the establishment of stable superlattice distortion rather than to the electron condensation. The transport anomalies may be caused by the pinning of the CDW rather than by the loss of the Fermi surface at T_1. This may also offer an explanation for the discrepancies in estimating the number of annihilated carriers by different experiments. We can estimate the carrier loss in CDW condensation by simply assuming $\sigma_j(0) \propto N(E_F)$, as discussed above, which leads to a relative decrease of $N(E_F)$ to $\sim$56% between 77 and 300 K.

The present measurements show that in the process of upper CDW condensation in $NbSe_3$ there exist four regimes. Below $\sim$100–130 K, a true 3D CDW phase is formed and completely pinned to the lattice in low fields (regime I). Regime II is characterized by coexistence of the pinned and mobile CDWs between $\sim$130 and $\sim$160 K. In regime III the fluctuated mobile CDW clusters contribute to a pseudogap extending to $\sim$260 K above which the CDW fluctuations become hardly detectable by tunneling experiments. The existence of these four regimes can also be demonstrated in the following way. The conductance of the $NbSe_3$ sample can be expressed by the formula $\sigma_s = ne\mu$, where n is the number of carriers and μ is the carrier mobility. Assuming $n \propto N(E_F) \propto \sigma_j(0)$, we get the mobility as a function of T as shown in Fig. 5. We see that while μ generally increases when T is lowered, some anomalous structure

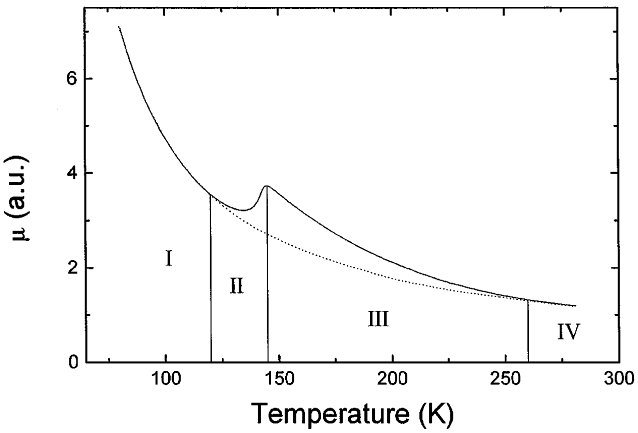

FIG. 5. The T dependence of the mobility (solid line), which can be divided into four regimes (see text). The dotted line is that expected for normal carriers. The excessive part can be ascribed in the contribution of CDW fluctuations.

exists. The reason is that in deducing μ, we implicitly take σ_s completely contributed by normal electrons, ignoring the role of mobile CDW clusters which make contribution to σ_s but not to σ_j. Assuming a smooth change of μ for the normal carriers, as shown in Fig. 5 by the dotted curve, an excessive part can clearly be seen. The excessive part can consistently be ascribed to the contribution of CDW fluctuations. In accordance with the behavior of 2Δ shown in Fig. 3, the contribution begins to appear at ~260 K and gradually increases with decreasing T until a little higher than $T_1 = 145$ K. Then the contribution decreases because of the increased fraction of pinned CDW. Below ~120 K, the CDW is completely pinned and the contribution of CDW to σ_s disappears.

In summary, by the measurements of tunneling spectra from 77 K to room temperature, the formation process of the upper CDW in $NbSe_3$ has been revealed. A pseudogap persists over ~260 K. $T_1 = 145$ K represents a true 3D phase transition and the pinning of the CDW, but the DOS at the Fermi surface as well as its temperature derivative continuously cross over T_1. The loss of carriers by CDW condensation takes place in a much wider temperature range than was thought.

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