Comparative spectroscopic study of $NiS_{2-x}Se_x$ single crystals

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By means of a low-temperature scanning tunneling microscope we have carried out a comparative study of the characteristic I-V (intensity vs voltage) curves, taken in tunnel and point-contact regimes, on $NiS_{2-x}Se_x$ single crystals, with $x=0.1$, 0.3, and 0.5 between 4.2 and 300 K. We show that for certain ranges of x a gap opens up in the density of states, which we ascribe to electron correlation effects that become prominent when Se is substituted for S at concentrations close to $x=0.5$. [S0163-1829(98)10639-2]

I. INTRODUCTION

Although interest in the physics of the metal-insulator transition (MIT) has been continuous in recent decades, the discovery of superconductivity and related MIT in some copper oxide based materials has led to increased attention to this phenomenon. The $NiS_{2-x}Se_x$ system is believed to be a good candidate to obtain valuable information about MIT and to shed light on the physics of the new superconductors.[1] This system has been rather extensively investigated[1–7] to explore the fairly rich phase diagram that is encountered for compounds with compositions in the range $0<x<0.75$ and for temperatures between 4.2 K and 300 K. The degree of metallicity tends to increase with rising x, and the degree of magnetic disorder tends to increase with rising temperature T. Of particular importance to the present investigation is the fact that in the range $0.44<x<0.55$ the resistivity ρ passes through a very pronounced maximum as T is raised.[2,4,8] This peak separates the low-temperature quasimetallic phase from the high-temperature semiconducting regime. In the temperature interval spanning the resistivity anomaly one also encounters an anomalous rise of the magnetization M with T. Both of these observations have been linked[8] to the opening of a gap in the density of states of the highly correlated electron system which arises from charge carrier interactions, as explained further below. This explanation was necessarily rather tentative, because it was based on indirect experimental evidence. It therefore seemed appropriate to attempt a more direct investigation based on tunneling and point contact spectroscopies for a test of the above hypothesis. The results of such a study are reported below.

II. EXPERIMENTAL AND BACKGROUND INFORMATION

Single crystals were prepared by procedures detailed elsewhere,[9] using Te as a flux. This avoids contamination of the specimens which occurs when the chemical vapor transport technique is employed for single-crystal growth. A common drawback of all the methods devised so far is the inability to control tightly and monitor the total anion to cation ratio r in this class of materials. Using presently available wet chemical or electron microprobe techniques r lies in the range $1.99<r<2.01$. As described in previous work, this uncertainty affects the reproducibility of the transport measurements and the detailed placement of the phase boundaries. In the present experiments, where only the main changes of the density of states with temperature are pursued, we consider that the uncertainty in r does not affect the conclusions of the study.

The experimental spectroscopic techniques have been previously described.[10,11] We employed a scanning tunneling microscope of standard design which can be operated over the range 2 K–300 K inside a ^{4}He cryostat to study the conductance behavior of nanosize junctions between different materials. The tip and sample electrode distance can be changed in a controlled manner by variation of the z-piezoelectric voltage. Pt and Au were used as tip counterelectrodes, with no detectable differences.

Current vs voltage, $I(V)$, characteristics were measured as a function of temperature over different locations on the samples to check on reproducibility; such curves are taken in 200 ms for a total of 1024 data points. The bias voltage was ramped typically between ± 500 and ± 1000 mV. Differential conductance curves, $dI/dV(V)$, were obtained by taking derivatives of the $I(V)$ data numerically. By varying the z-piezovoltage (which controls the electrode separation and the size of the contact region) we covered both the vacuum tunneling and point-contact spectroscopic regimes, with resistances between electrodes ranging from MΩ to several Ohms. The changes in the conductance curves, while the electrodes were brought together, were monitored in a series of measurements on one small area of the sample. This allowed us to monitor the changes in the conduction regime: i.e., from tunneling, for which the $dI/dV(V)$ curves provide information about the electrode electronic density of states, $N(E)$, to the point contact regime, in which mainly the inelastic scattering processes are probed.

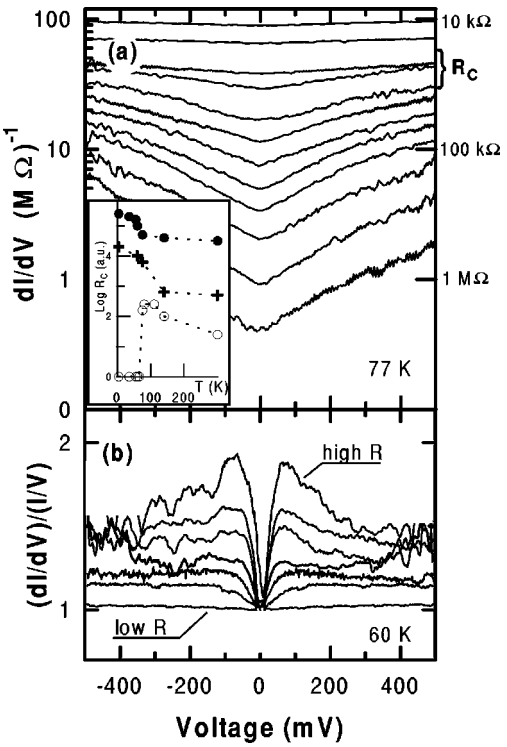

FIG. 1. (a) High-temperature conductance behavior for the $x=0.1$ sample. The change of shape denotes the transition of the conductance regime from tunneling to point contact as the resistance is decreased. Approximate contact resistance, R_C, is indicated. (b) Logarithmic derivative of $I(V)$ curves obtained at 60 K, showing the existence of a gap in the tunneling regime. Inset: Evolution with temperature of the estimated value of R_C for the three samples studied ($x=0.1$, solid circles; $x=0.3$, crosses; and $x=0.5$, open circles). Relative variation from the value at 300 K, curves are shifted for clarity.

Our ability to control the electrode separation distances during the $I(V)$ measurements permitted us to determine the resistance, R_C, marked in Fig. 1(a), at which electrode contact is first established. By gentle manipulation it was possible to probe contact areas of similar size in all measurements. Typically, R_C values varied by 20% to 30% for a given sample and temperature. As shown in other investigations,[12] the relative variations of this resistance as a function of temperature properly reflect the change of bulk resistivity with temperature.

We emphasize again that all the figures presented in this work are representative of the behavior observed in many different measurements on different spots on the samples surface.

III. EXPERIMENTAL RESULTS

In the inset to Fig. 1 we show the resistivities, R_C, of the three samples with $x=0.1$, 0.3, and 0.5 as a function of temperature. These results compare favorably and interleave properly with those[8] obtained by the standard four-probe technique. The agreement between the present scanning tunneling microscope (STM) and the four terminal measurements validates the use of our STM measurements in providing correct information about electron transport in these samples. One should note the semiconducting characteristics of the samples with $x=0.1$ and 0.3 and the quasimetallic characteristics of the sample with $x=0.5$ at low temperatures. This sample exhibits an increase in resistivity by 2.5 orders of magnitude in the range 55 K–75 K and semiconducting characteristics at higher temperatures. All of this accords with earlier work.[2,4,6,8]

According to the literature, the samples with $x=0.1$ and $x=0.3$ present a very similar behavior of the resistivity as a function of temperature, and concerning the phase diagram they present the same magnetic transitions. We have observed also a similar behavior in our spectroscopic measurements. Then, we will focus on the properties of the samples with $x=0.1$ and $x=0.5$, to compare their electronic density of states, based on the very different changes of their resistivities with temperature.

Typically, as shown in Fig. 1, one observes U- or V-shaped conductance curves in the tunneling regime, while the point-contact measurements lead to almost ''flat'' responses essentially independent of the applied voltage. Deviations from this behavior provide information on the different types of inelastic scattering processes occurring in the contact region.

The sample with $x=0.1$ is a semiconductor over the entire temperature range under investigation. The material is paramagnetic for $T>40$ K, antiferromagnetic for $25\ \mathrm{K}\leqslant T\leqslant 40$ K, and weakly ferromagnetic for $T<25$ K.[5,6] A typical set of conductance curves at high temperatures ($77\ \mathrm{K}<T<300$ K) is shown as a semilogarithmic plot in Fig. 1(a). This permits us to compare junctions with resistances ranging from the high tunneling values to those of the contact regime. Under high resistance (tunneling) conditions the variation in differential conductance from high bias $[G(V\ \mathrm{max})]$ to zero bias $[G(0)]$ is about one order of magnitude, a clear indication that the compound is nonmetallic. However, there is no obvious signature of a gaplike structure in the conductance spectra in this temperature range; this very likely indicates that the thermal energies are comparable to the gap energy (see also below). The almost flat spectra in the contact regime indicate that within our resolution we do not observe the effects of any relevant scattering processes. On lowering the temperature, deviations from the symmetric V-shaped spectra appear at 60 K. We observe an extra dip close to zero bias and a slight asymmetry with respect to the sign of bias voltage in the low-conductance spectra. The effect is enhanced in the logarithmic derivative plots, $(dI/dV)/(I/V)$ vs V, of Fig. 1(b). This leads to an estimated gap size of $\Delta\simeq 60$ meV, indicative of the semiconducting properties of the material. When the tip is pressed against the sample, the conductance spectra become almost Ohmic, as they do at higher temperatures.

For $T<52$ K, where the sample becomes antiferromagnetically ordered, one still encounters V-shaped characteristics in tunneling, with very low conductance at zero bias, but as the resistance is diminished toward the transition between conduction regimes ($R\sim 50\ \mathrm{k}\Omega$) the spectra evolve into a well defined, rounded gaplike structure. The edges are now marked by a broad peak that increases in height as the resistance is lowered. As shown in Fig. 2, the location of the peak positions varies between 100 meV and 150 meV. The gap features survive to the highest measurable conductances; we never encountered the flat conductance regime. These peaked

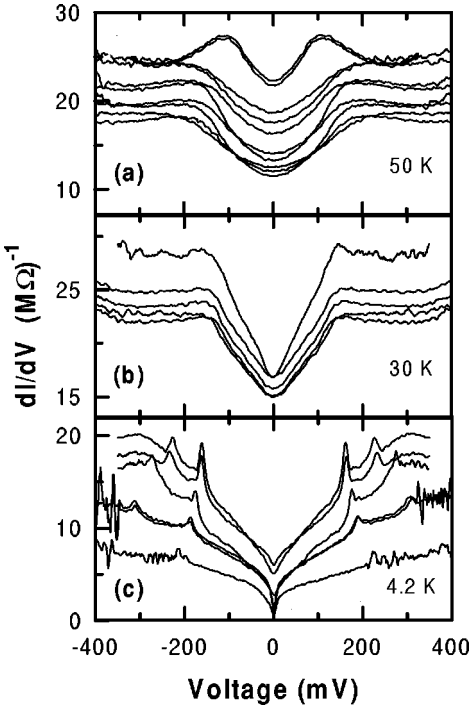

FIG. 2. Conductance curves obtained in the point-contact regime for the $x=0.1$ sample at 50 K, 35 K, and 4.2 K (phases with magnetic order).

spectra obtained in the point-contact regime may be attributed to inelastic scattering processes associated with magnetically ordered states that develop at low temperature.

At still lower temperatures one encounters very similar features, except that the profiles are sharpened. The U-shaped valley at zero bias changes to a deeper V-shape at 30 K [Fig. 2(b)], and very sharp small peaks appear in the 4.2 K spectra at about 200 meV [Fig. 2(c)]. These peaks, which increase their height with increasing conductance, may be originated by the type of inelastic processes mentioned above.

We next consider the $x=0.5$ specimen; as shown in the inset to Fig. 1, this specimen changes, when increasing temperature, from a quasimetallic to a semiconducting regime near 60 K. Typical conductance data taken at 77 K, 97 K, and 110 K are shown in Fig. 3. These spectra exhibit the usual V-shaped background and a gaplike structure around zero bias. In most cases there also occurs a slight asymmetry in the conductance with respect to the sign of bias voltage, especially at the lower temperatures. The tunneling curves resemble the characteristic ones typical of conventional semiconductors. A gap feature of about 100 meV is encountered. It is interesting to note that the gap appears to diminish with decreasing temperature; this matter is discussed further below.

Curves obtained in the point-contact regime, shown only for 110 K, are essentially flat with no indication of inelastic scattering processes. The asymmetry effect and the similarity with respect to ordinary semiconductors are best seen plotting current and conductance vs voltage curves. Figure 4 shows a set of representative curves obtained at 77 K for high junction resistances. The clear asymmetry indicates that this sample is a p-type semiconductor.

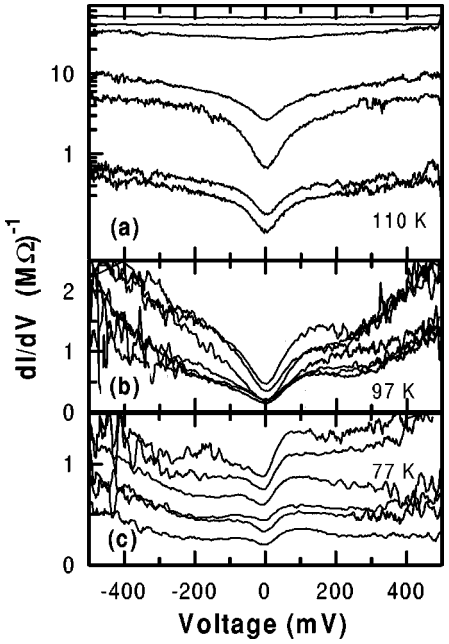

FIG. 3. Typical conductance evolution in the $x=0.5$ sample at high temperatures. (a) 110 K, (b) 97 K, (c) 77 K.

As temperature is decreased, the gap shrinks to a value of 25–50 meV, and usually another dip appears at zero bias. In Fig. 5 we display several examples of conduction characteristics of the sample $x=0.5$ at 4.2 K. Here, the situation is quite different from that which prevails at higher temperatures. Figure 5(a) displays a clear gaplike structure, with peaks at ± 60 mV, together with a sharp peak at $V=0$ which develops as the junction resistance is decreased toward 10 kΩ. This feature is rendered more prominent in another set of measurements, taken at a different spot on the sample, shown in Fig. 5(b), where a structure of width 80 meV ap-

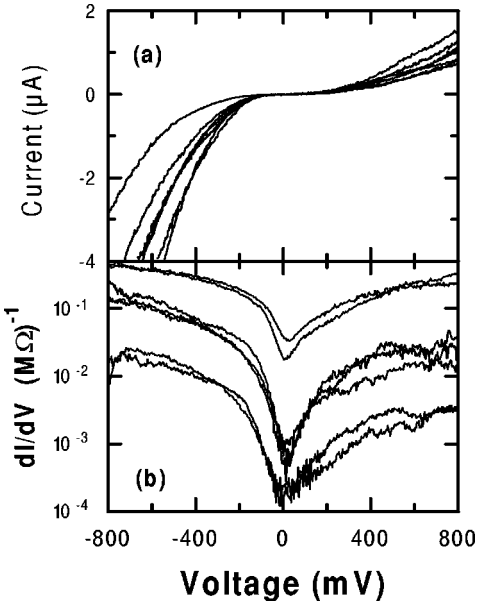

FIG. 4. (a) I vs V curves, for the $x=0.5$ sample, obtained in the tunneling regime at 77 K, showing typical semiconducting behavior. (b) Conductance vs voltage curves corresponding to I-V curves showed in (a).

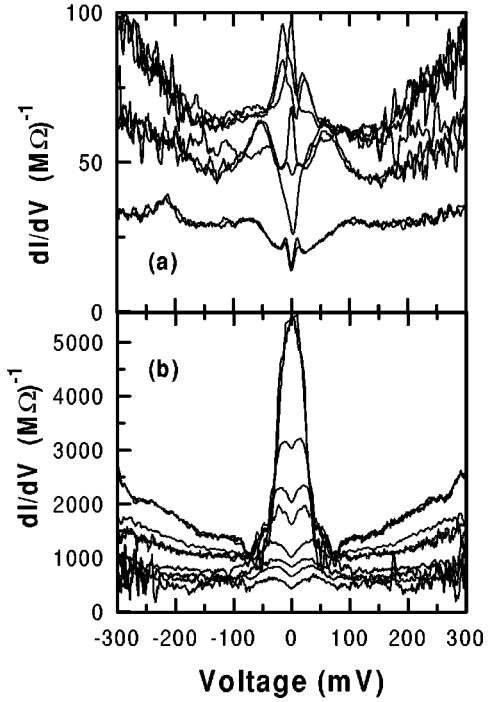

FIG. 5. Conductance curves obtained at 4.2 K in the $x=0.5$ sample showing the development of the maximum in conductance at zero bias.

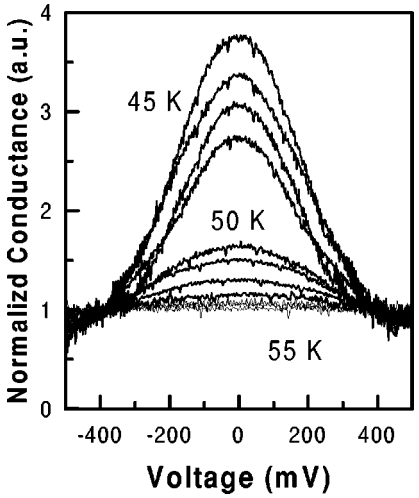

FIG. 6. Evolution of the conductance curves in a contact as temperature is varied between 45 K and 55 K, showing the development of the maximum of conductance at zero bias, which denotes the transition to a metallic state at low temperature in the $x=0.5$ sample.

pears close to zero bias, whose height increases dramatically as the contact resistance is decreased. Such enhancements are always observed at low temperatures but vary with the location of the contact on the sample. As can be seen in the higher curves of Fig. 5(a), in some cases slight variations of the contact are critical in order to observe the appearance of the conductance peak at zero bias. The phenomenon generally appears at contact resistances less than 10 kΩ, and for voltages below ± 200 mV.

The effect may therefore be linked to the transition to the quasimetallic state exhibited in the inset to Fig. 1, and noted in prior measurements.[8] However, the spectra suggest that this is not the standard metallic state with $N(E) \sim N(E_F)_{\text{metal}}$ over a wide range of energies. Rather, the data suggest the presence of a very narrow band of states close to the Fermi level, located inside the gap observed at higher temperatures. A model of this type was shown by Matsuura *et al.*[3] and by Yao *et al.*,[8] and is discussed in a recent work by Watanabe and Doniach.[1]

As already stated, the relative height of the central structure in the dI/dV curves increases as we attain higher conductance values (i.e., a larger size of the contact). We have observed the same behavior in different materials,[11] and it is a common situation when inelastic scattering processes are involved in point-contact spectroscopy measurements.[12] In this case, the larger the ratio a/l (with a the radius of the contact and l the inelastic electron mean free path), the greater will be the information about inelastic processes that appears in the conductance spectra. This is usually observed in measurements of the phonon structure in normal metals, and it is well known that point-contact spectroscopy can furnish distinct information on electron-phonon, electron-magnetic impurity interactions, or interactions with energy levels associated with crystal-field splittings.

Figure 6 shows the variation in conductance for a fixed contact to the $x=0.5$ sample when temperature is varied between 45 and 55 K. We clearly observe an increase of the conductance at zero bias with diminishing temperature, which permits us to set the range 50–52 K as the transition from the metallic to the semiconducting regime, in reasonable agreement with the R_C vs T data of Fig. 1.

IV. DISCUSSION AND CONCLUSIONS

The above experiments provide direct experimental evidence for the presence of a gap in $NiS_{2-x}Se_x$ under conditions where the material is a semiconductor. Depending on circumstances, the gap generally falls in the range 60–150 meV, consistent with values previously cited on the basis of optical[13] and conductivity[8,14] studies. The compound with $x=0.5$ is particularly interesting with respect to the very large rise of resistivity with temperature between 50 K and 70 K. It was argued[8] that correlation effects among electrons favor a certain degree of electron localization. In a half-filled band of primarily e_g states, the electrons, in the limiting case of total localization, have an entropy of $k_B \ln 2$ (k_B is the Boltzmann constant), whereas the entropy of the itinerant charge carriers is much less. This localization involves a further narrowing of the already narrow, highly correlated band, which should lead to the opening of a band gap, as manifested by the very marked increase in resistivity of samples of compositions $0.44 \leqslant x \leqslant 0.55$ with T over a limited temperature range. However, such evidence was at best indirect. The above hypothesis is therefore considerably strengthened by the present measurements on the $x=0.5$ sample. These provide direct observations of a gap which diminishes with

temperature in the indicated range. However, according to present measurements, the gap never closes completely; rather, new, metalliclike states develop inside the gap, which can be correlated with the quasimetallic characteristics of the compound below 50 K.

ACKNOWLEDGMENTS

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