Effect of heating and rapidly quenching $NbSe_3$ crystals

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We have heated single crystals of $NbSe_3$ to 620 °C for about 4 min and then rapidly, in less than 1 sec, quenched them to room temperature. We find that the resistive anomalies associated with the charge-density-wave transition have been completely suppressed. The crystals exhibit metallic behavior over the entire temperature range from 300 to 7.5 K. There appears to be no electric field dependence of the resistivity at 50 K to fields up to a few hundred millivolts/cm. Quantitative energy-dispersive x-ray spectroscopy suggests that quenching $NbSe_3$ crystals changes them to $NbSe_2$. This is further verified by following the temperature dependence of the resistance to lower temperatures, where a superconducting transition is seen in the quenched crystals at 7.2 K. This corresponds to the superconducting transition seen in crystals of $2H$-$NbSe_2$. Thus it appears that by rapidly quenching $NbSe_3$ from 620 °C one is able to form $NbSe_2$ while maintaining a needlelike morphology.

INTRODUCTION

Recently it has been found that thermally quenching $NbSe_3$ samples from 620 °C to room temperature induces switching in the I-V characteristics.[1] Switching samples have been shown to produce a chaoticlike behavior which is not present in nonswitching samples. Possible freezing in large numbers of defects, incoherent domain structures, etc., have been attributed to the quenching process. Low-temperature quenching experiments by Tritt *et al.*[2] have shown that the Fermi surface is very susceptible to changes in the metastable configuration of the charge-density wave (CDW). In that work, after rapidly quenching the samples from 100 to 4.2 K, spontaneous changes in the resistance, magnetoresistance, and the frequency of the Shubnikov–de Haas oscillations were observed.

$NbSe_3$ has two CDW transitions which occur at $T = 144$ and 59 K. Peaks in the resistance as a function of temperature occur below these temperatures. The overall behavior of $NbSe_3$ is metallic, or rather semimetallic. As impurities are added to $NbSe_3$ the CDW's are gradually destroyed[3,4] and the residual resistance ratio (RRR) $\mathcal{R} = R(300\text{ K})/R(4.2\text{ K})$, decreases. Radiation damage also decreases the RRR,[5] eventually making $NbSe_3$ lose its metallic behavior. Applied pressure reduces the CDW transition temperature.[6] Both impurities and pressure cause $NbSe_3$ to become superconducting below 3 K.[4,6] The application of uniaxial stress[7] or a magnetic field[8] enhances the resistive anomalies associated with the CDW transitions.

In an attempt to study the nonlinear properties of switching samples, we have quenched $NbSe_3$ from 620 °C to room temperature. Instead of inducing switching in our samples, we have found that a very rapid quench of $NbSe_3$ from 620 °C to room temperature destroys all signs of the resistive anomalies associated with either CDW transition.

PREPARATION OF SAMPLES

Bundles of $NbSe_3$ crystals were placed in 3-mm quartz tubes which were evacuated with a roughing pump and then sealed. A tube furnace was preheated to 620 °C. The quartz tubes containing the $NbSe_3$ were placed in the large tube of the furnace for 4 min. At that point they were dropped into water at room temperature. The quenching took less than 1 sec as judged from the length of time a sizzle was heard.

CHARACTERISTICS OF RAPIDLY QUENCHED $NbSe_3$

Figure 1 shows the normalized resistivity of unquenched and our rapidly quenched $NbSe_3$ samples. It is immediately obvious upon comparing the curves that the

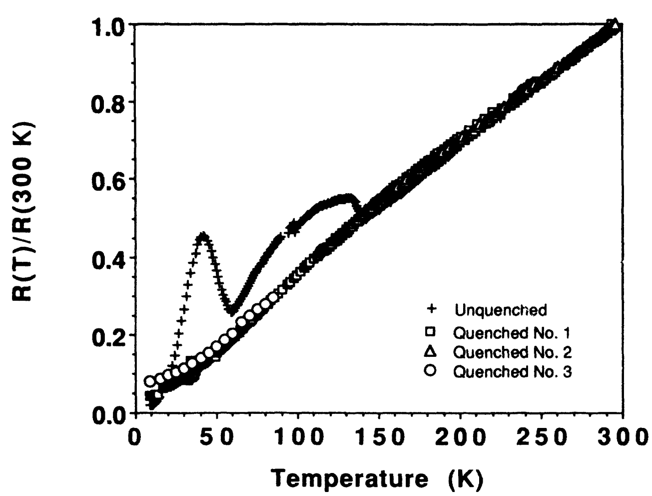

FIG. 1. Normalized resistivity as a function of temperature for unquenched and rapidly quenched $NbSe_3$. Note that there is no sign of either CDW resistive anomaly in the quenched samples. The measuring currents were all less than 0.08 mA.

quenching has drastically affected the CDW anomalies. The room-temperature resistivity is the same order of magnitude for the quenched and unquenched samples. The quenched samples look like $NbSe_3$; they have a metallic sheen, although they are darker, and they still have a needlelike morphology. They have become much more brittle, however. All of our rapidly quenched samples show these characteristics. We have also found that near 50 K the quenched samples show no sign of nonlinear conductivity up to electric fields of several hundred mV/cm.

In an attempt to determine whether we have modified the stoichiometry of the crystals by our quenching process, we have performed quantitative energy-dispersive x-ray spectroscopy (EDXS) using a scanning electron microscope. We used several nonquenched $NbSe_3$ crystals as a standard to obtain the Nb to Se ratio of 1:3, within 10%. Having obtained a standard we then looked at the quenched samples. We found that within 20% all the quenched samples that we studied in this manner had a Nb to Se ratio of 1:2. No other elements, to several atomic percent, were found in our analysis.

Figure 2 shows the normalized resistivity as a function of temperature below 8 K for our quenched samples. As can be seen, a sudden resistance drop occurs at approximately 7.2 K. This is in the range of temperatures where $2H$-$NbSe_2$ undergoes a superconducting transition.[9,10]

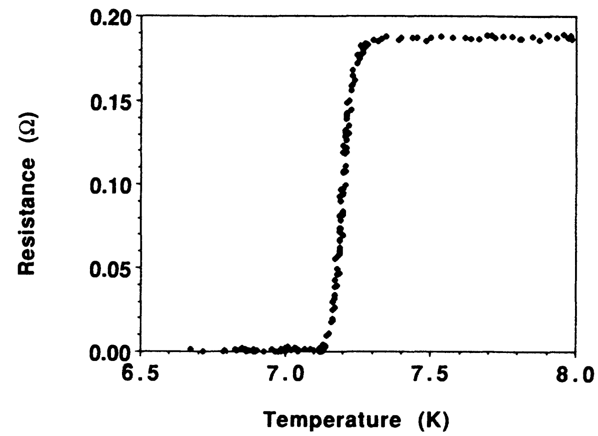

FIG. 2. The low-temperature resistance as a function of temperature for a representative, rapidly quenched $NbSe_3$ sample. A superconducting transition occurs at 7.2 K.

DISCUSSION OF RESULTS

From EDXS and the low-temperature resistance measurements it appears that we have transformed $NbSe_3$ crystals into $NbSe_2$ crystals via briefly heating at 620 °C and then rapidly quenching to room temperature. These crystals remain needlelike although they are more brittle. Dalrymple *et al.*[10] have seen that there is a temperature range during vapor transport growth where both $NbSe_2$ and $NbSe_3$ can be formed, providing excess Se is present. They found that by rapidly quenching the material to room temperature the diselenide was formed, whereas a slower cool down led to the triselenide. However, they still obtained platelets for their $NbSe_2$ crystals. Thus the rapid quenching appears to catch a metastable morphology of $NbSe_2$.

The switching seen in some $NbSe_3$ samples has been suggested to be due to defects or inhomogeneities.[11] Perhaps our results show that the type of defects induced in the switching samples via heating and then quenching the $NbSe_3$ could be regions of a different Nb-Se compound like the $NbSe_2$ which we are reporting.

CONCLUSIONS

We have shown that heating $NbSe_3$ crystals and then very rapidly quenching them results in their transformation to $NbSe_2$. These crystals of $NbSe_2$ do not have their normal morphology; instead of being platelets they maintain the needlelike characteristics of $NbSe_3$.

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