Superconductivity of the Linear Trichalcogenide NbSe₃ under Pressure

P. Monceau, J. Peyrard,^(a) J. Richard, and P. Molinié^(b)

Centre de Recherches sur les Très Basses Températures, 38042 Grenoble-Cedex, France (Received 23 February 1977; revised mansucript received 12 May 1977)

We show that the linear compound NbSe₃ becomes superconducting under pressure. We have measured the initial slope of the magnetization of NbSe₃ as a function of pressure down to temperatures as low as 50 mK. A very small pressure is necessary in order for the superconductivity to occur. T_c is strongly pressure dependent. We find that the initial slope $dT_c/dP = 0.6$ K/bar. We attribute this huge variation of T_c to changes in the band structure induced by pressure.

Until recently very few measurements of the electronic properties of transition-metal trichalcogenides TX_3 (T: Ti, Zr, Hf, Nb, Ta; X: Se, S, Te) have been reported. All these compounds have structures made up of infinite chains of trigonal prisms TX_6 extending parallel to the *b* axis of their monoclinic cell.¹⁻³ The trichalcogenides of the group-IV transition elements as well as the sulfide compounds of group VB are semiconductors. Only TaSe₃^{4,5} and NbSe₃⁶ show a metallic behavior from room temperature down to the helium range. In particular, NbSe, has very spectacular properties^{6,7}: NbSe₃ exhibits two phase transitions at $T_{c1} = 145$ K and $T_{c2} = 59$ K where a sharp increase in resistivity occurs. These anomalies in resistivity were ascribed to the formation of charge-density waves (CDW). Applying pressure causes the critical temperature of CDW formation to decrease.⁷ It was also shown that the resistivity anomalies are strongly nonlinear⁸ -a small electric field ($\simeq 0.5 \text{ V/cm}^{-1}$) is enough to cause the breakdown of these anomalies. Here we have extended the pressure measurements at lower temperatures and we report on the discovery that NbSe₃ becomes a superconductor under pressure.

Our samples of NbSe₃ were prepared by the direct reaction of Se and Nb in stoichiometric proportions.³ The mixture is sealed in a quartz tube under vacuum and heated to 700°C for 15 days before quenching. NbSe₃ crystallizes in the form of fibers which can be easily separated. Six NbSe₃ groups form the unit cell. Direct bonding does exist between the two nearest Se atoms in the base of each prism. From one chain to the next the atoms are translated by a 0.5 unit cell; the distance between Nb atoms along the *b* axis is 3.478 Å and varies from 4.45 to 4.25 Å in the *a-c* plane. This "one-dimensional" (1D) structure explains why NbSe₃ crystals are fibrous. This structure is to be compared with that of transition-metal dichalcogenides of type 2H-NbSe₂ where the NbSe₆ prisms are joined side by side to form infinite 2D layers.

The dc electrical conductivity parallel to the fibers lies between 1250 and 1700 (Ω cm)⁻¹ at room temperature,⁷ in good agreement with the microwave conductivity at 9.3 GHz measured by a cavity perturbation technique.⁹ We have also measured the microwave transverse conductivity at room temperature and have found it to lie between 1.3 and 3.8 (Ω cm)^{-1.9} This corresponds to an anisotropy at room temperature of between 350 and 1200.¹⁰ It has also been shown that TX_3 compounds retain the chain structure with intercalation of Li during reaction with *n*-butyl-lithium in hexane yielding a ternary phase of Li_3TX_3 .¹¹⁻¹³ The inclusion with lithium forces an expansion normal to the chains but the distance along the baxis is essentially maintained. However, the insertion of lithium breaks the polychalcogenide bonds of the original structure and the process is not reversible. Its structure, its large electrical-conductivity anisotropy, and the fact that intercalation maintains the chain structure are properties which bring us to include NbSe₃ in the group of quasi-1D conductors.

We have measured the initial susceptibility of NbSe₃ under pressure in an adiabatic refrigerator apparatus between 50 mK and 10 K. Typically 30 mg of fibrous strands of NbSe₃ were set in a beryllium copper clamped piston and cylinder device using Teflon as the pressure medium. Pressure was applied at room temperature. Because of the different expansion coefficient between Teflon and beryllium copper there is a decrease of the pressure inside the cell during cooling. We have obtained the pressure at the helium range by measuring the decrease of the critical temperature of indium under pressure (assuming¹⁴ $\Delta T_c/\Delta P = -44.5 \times 10^{-3}$ K/kbar) set in the same cell but replacing the NbSe₃ sample. The increase of the



FIG. 1. Variation of the initial slope of the magnetization of NbSe₃ as a function of temperature for different pressures. The different values of χ at low temperature for 0.5 kbar, 2.25 kbar, and higher pressure are due to the variation of the demagnetization coefficient of the superconducting sample under pressure. The dotted curve is the initial susceptibility of a second sample with the same weight but a different demagnetization coefficient. We define T_c as the middle of the variation of χ with T.

width of the superconducting transition gives also the pressure distribution inside the cell (thus, for 10 kbar at room temperature the pressure at helium range is 6.5 kbar and the pressure distribution is about ± 0.4 kbar). Figure 1 shows the initial slope of the magnetization versus temperature for different pressures. The residual susceptibility χ above 3 K is attributed to the presence of NbSe₂ impurities around the NbSe₃ fibers: This susceptibility goes to zero above $T_c = 7.2$ K, the critical temperature of NbSe₂. At ambient pressure, NbSe₃ is not superconducting down to 50 mK; but under pressure, it becomes fully superconducting. The measured susceptibility χ is in good agreement with the theoretical value of the susceptibility in the superconducting state, $-(4\pi)^{-1}V/(1-n)$, where V is the volume of the sample and n the demagnetization coefficient. The different values of χ at low temperatures for 0.5 kbar, 2.25 kbar, and the higher pressures can be taken into account by the variation of n under pressure. We define T_c as the middle of the variation of χ with T. The variation of T_c with pressure is plotted in Fig. 2. T_c strongly depends on P: T_c first increases with P at low values of the pressure with a slope $dT_c/dP = 0.6$ K/kbar, then it seems to saturate. We have not observed any irreversibility in cycling the pressure; after releasing the pressure, the sample indicates no superconducting properties at ambi-





ent pressure down to 150 mK. Experiments are under way to study the possibility of uniaxial effects in the occurrence of superconductivity in NbSe₃.

We have also measured the susceptibility under pressure of $TaSe_3$. This compound has a very similar structure⁴ to NbSe₃ but with only four $TaSe_3$ groups in the unit cell. The resistivity at room temperature is the same as for NbSe₃. The temperature variation exhibits a metallic behavior between 300 and 1.2 K without any anomaly.⁵ The measurements of susceptibility at 50 mK at ambient pressure and under 6.5 kbar have shown no trace of superconductivity in this compound.

A general characteristic of 2D and 1D solids is in their instability towards the formation of CDW states in which the lattice and the induced modulation of the electron charge density freeze into a superlattice structure which create an energy gap at the Fermi level.^{15,16} For 1D conductors, because of the topology of their Fermi surface, this instability transforms the material into a semiconductor. The 1D conductors such as KCP or TTF-TCNQ show 1D distortions along the chains in the metallic range at room temperature which were observed by diffuse scattering of x rays^{17,18} or elastic neutron diffraction.^{19,20} These 1D distortions are weakly coupled by the interchain coupling. When the temperature is lowered, the transverse coherence length increases, indicating a 3D ordering. For systems of higher dimensionality the onset of CDW is less drastic and results in small anomalies in resistivity. Experimentally the existence of CDW has been established in the layered dichalcogenides such as 2H-NbSe₂ and 2H-TaSe₂.¹⁶

As explained above, NbSe₃ has 1D properties at high temperature. However, the metallic phase at low temperature has the characteristics of a semimetal. We have observed a very large transverse magnetoresistance and preliminary experiments show Shubnikov-de Haas oscillations of the resistivity with the magnetic field.²¹ The effective dimensionality at low temperature of NbSe. may be 2D or 3D. $NbSe_3$ is liable to be compared to the charge-transfer salt hexamethylenetetraselenafulvalene-TCNQ. This compound is the best organic conductor known²² [$\sigma = 1800 \pm 400$ $(\Omega \text{ cm})^{-1}$] and has a metallic behavior down to 45 mK. A semimetallic behavior under pressure was observed by magnetoresistance.²³ At room temperature, 1D distortions were observed by diffuse x rays²⁴ but in contrast with TTF-TCNQ these distortions have transverse components in both directions.

To enhance T_c , assuming the McMillan relation,²⁵ it is necessary to increase the electronphonon coupling constant $\lambda = N(0)g^2/M\langle\omega^2\rangle$, where N(0) is the density of states at the Fermi level. $\langle \omega^2 \rangle$ the average phonon frequency, and g the electron-phonon matrix element. It may be possible to have phonon modes which soften under pressure as was proposed by Testardi²⁶ to explain the pressure dependence of T_c in A15 compounds. However this soft-mode model predicts a maximum of T_c when $T_{CDW} \approx T_c$ which was never observed in layered compounds. Before ruling out completely this possibility for NbSe₃, it would be necessary to perform experiments at higher pressures. Another possibility for the enhancement of T_c is the increase of N(0) under pressure by reducing the amplitudes of the gaps opened at the Fermi surface by the CDW's.²⁷ However we have observed a huge variation of T_c under pressure, whereas the temperature of the onset of the CDW T_{c2} and the amplitude of the resistive anomaly have only slightly changed⁷ (e.g., for 1.5 kbar T_c =0.85 K and T_{c2} has changed from 59 K to 53 K and the anomaly decreases by 55%). Such a large effect of pressure on T_c can be more satisfactorily explained through a pressure-induced bandstructure change. Because of the semimetallic behavior of NbSe₃ at low temperature, the Fermi level is strongly dependent on external parameters—in particular, pressure. Both effects, suppression of CDW and change of the band structure, may be associated in enhancing T_c but we suspect that the latter is the more important.

In the course of these experiments we had expected TaSe₃ to become superconducting with pressure mainly because it behaves like a normal metal. This is not the case, but it must be kept in mind that T_c for the dichalcogenide 2H-TaSe₂ is very small ($T_c = 0.15$ K)²⁸ and its pressure dependence $dT_c/dP < 1.3 \times 10^{-5}$ K/kbar.²⁹ The electron-phonon interaction is probably too weak to make TaSe₃ superconducting (the molar weight of Ta is much higher than that of Nb), or, because of a different unit cell, the Fermi surface may be much less pressure dependent.

In summary, we have found NbSe₃ to be superconducting under pressure. NbSe₃ can be described as a 1D conductor at room temperature, but has a semimetallic behavior at low temperature. The appearance and the variation of T_c with pressure is attributed to a change of the band structure. At this point more experimental and theoretical work is necessary to obtain a full understanding of the properties of this compound.

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^(a)Also at Service National des Champs Intenses, Centre National de la Recherche Scientifique, BP 166 X, 38042 Grenoble-Cedex, France.

^(b)Permanent address: Laboratoire de Chimie Minérale, 44037 Nantes-Cedex, France.

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