

Superconductivity in Ultrathin NbSe₂ Layers

R. F. Frindt*

Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada

(Received 7 December 1971)

The superconducting resistive transition of the layer compound NbSe₂ has been observed for crystals a few layers thick. The T_c decreases as the crystal thickness is reduced below six NbSe₂ layers, and a T_c of 3.8°K is predicted for a single layer. No significant increase in the transition width is observed as the number of NbSe₂ layers is reduced. The results are compared to recent work on intercalated layer compounds.

There is at present considerable interest in the possibility of "two-dimensional" superconductivity occurring in layer compounds such as TaS₂ and NbS₂, where the layers have been separated by organic molecules by as much as 57 Å.¹ As a different approach to the problem of two-dimensional superconductivity, we report here on some measurements of the superconducting transition temperature for ultrathin single crystals of the layer compound NbSe₂.

The NbSe₂ crystal is made up of stacks of NbSe₂ layers, each layer consisting of a sheet of Nb atoms between two sheets of Se atoms. The separation of the Nb sheets is 6.3 Å. Because of the weak bonding between adjacent Se layers, the crystals are easily cleaved. We have studied the 2H modification of NbSe₂, where there are two layers per unit cell, giving a unit cell dimension (c_0) of 12.6 Å.² The superconducting transition temperature of 2H-NbSe₂ is 7°K.³ Our single crystals were grown by standard transport reaction procedures, using iodine as the carrier.⁴

We have prepared thin crystals on three different substrates, namely, mica, epoxy, and fused quartz. Thin crystals are obtained by sticking a crystal onto the substrate and peeling it away until a very thin crystal remains on the substrate. In the case of mica and quartz substrates, the crystals stick because of strong surface forces.

The resistive transition for different thicknesses of NbSe₂ single crystals is shown in Fig. 1. The sample resistance is shown as ohms per square which is the resistance of a square sample of a given thickness. Since the crystal thickness is inversely related to the resistance per square, it can be seen that T_c decreases as the thickness is reduced. The steps in curves *a* and *c* show that these samples consisted of different thicknesses: Here the resistance per square refers to the thinnest region. Small steps slightly above 7.0°K are seen with samples *a* and *c*. These are due to a thick part of the sample going superconducting and can serve as a temperature calibra-

tion. The widths of the resistive transition, measured from the 10 and 90% points, are in the range 0.2 to 0.3°K and show no significant change with decreasing thickness. The widths for unstrained bulk crystals are in the range 0.1 to 0.2°K. The sample currents were along the layers in all cases and precautions were taken to ensure that the low-current resistive transition was measured (shifts in T_c of 0.1°K were observed for current densities of 10⁴ to 10⁵ A/cm²).

A T_c slightly above 7.0°K in Fig. 1 results from strain introduced by the substrate on cooling. We have observed a T_c as high as 7.5°K and transition widths of ~1°K for some samples on epoxy (sample compression). For crystals on a quartz substrate (sample tension), the T_c is reduced to about 6°K, and similar resistive steps are seen with decreasing crystal thickness. Mica appears to be a fairly good substrate match for NbSe₂. The strain effects noted here are in qualitative agreement with the observed increase in T_c for NbSe₂ under hydrostatic pressure⁵ (although c -axis strain, as well as a -axis strain, is occur-

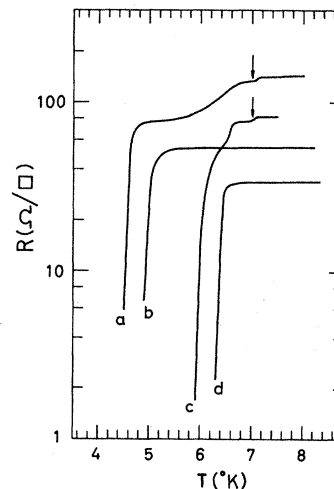


FIG. 1. The superconducting resistive transition for various thicknesses of NbSe₂ crystals. The arrows indicate the T_c for unstrained bulk crystals. Curve *a*, epoxy substrate; curves *b*, *c*, and *d*, mica substrate.

ring for samples under hydrostatic pressure). Since the shift in T_c with decreasing thickness is observed for very different states of sample strain, we conclude that the effect is not due to strain. We have observed changes in T_c for some samples after several coolings; however, as examples of reproducibility, the same resistive transition was observed for sample *b* after three days and for sample *c* after a period of 22 days. The experiments were all carried out in British Columbia air, the samples being stored in a dark dessicator when not in use.

The thickness of a crystal or film may be obtained from the resistance, if the resistivity is known. We have measured the temperature dependence of the resistivity for samples *b* and *d* in Fig. 1 and find that the ideal resistivity is very similar to the behavior of the ideal resistivity for bulk NbSe₂ crystals,^{6,7} namely, linear for $T > 100^\circ\text{K}$ and $\sim T^2$ in the range 20 to 40°K. The resistance ratio $R(300^\circ\text{K})/R(8^\circ\text{K})$ was 14 for sample *b*, 11 for *c*, and 15 for *d*, as compared with 16 for our bulk crystals. It thus appears that there is no significant size effect on the resistivity of these samples. This is not too surprising for a layer structure such as NbSe₂, which has perfectly smooth surfaces⁸ and where the carriers would tend to remain with a layer. Because strain can affect the resistivity at low temperatures, we have used the 300°K resistivity of $160 \times 10^{-6} \Omega \text{ cm}$ for our bulk crystals, and the resistance per square at 300°K to calculate the thickness of the thinnest parts of samples *b*, *c*, and *d* in Fig. 1, and expect this to give reliable values. With sample *a* however, a resistance ratio of only 3 was observed for the thinnest region (as compared with a value of 11 generally observed with epoxy substrates), so that a thickness obtained from the resistivity is no longer reliable. We have also observed a T_c of 4.6°K for a similar sample on epoxy with a resistance ratio of 3. We intend to study the resistivity of such samples in greater detail; however, it is safe to say that both of these crystals are thinner than sample *b*. The thicknesses calculated from the resistivity are in the range 30 Å and less. Such thicknesses, although small, have been obtained with crystals of WSe₂⁹ and also with MoS₂, where the thickness was measured using the electron microscope.⁸

The dependence of T_c on crystal thickness is shown in Fig. 2. The T_c values were taken for 50% of the normal resistance for the thinnest regions of Fig. 1. It is seen that T_c starts to drop significantly from 7.0°K at a thickness of about

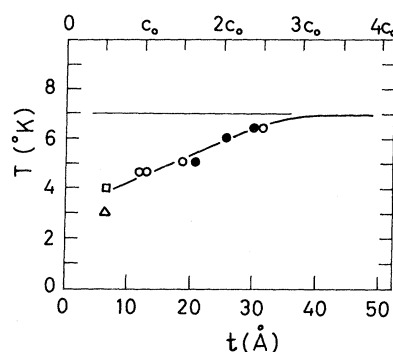


FIG. 2. The superconducting transition temperature of NbSe₂ plotted against calculated crystal thickness t (filled circles); the open circles give the crystal thickness to the nearest multiple of the single-layer thickness. The T_c for intercalated NbS₂ (square) and intercalated TaS₂ (triangle) are also shown.

40 Å, or three unit cell layers. Now the crystal thickness must be multiples of 6.3 Å, the thickness of a single layer. The open circles in Fig. 2 show the thicknesses as multiples of 6.3 Å; a thickness of 12.6 Å has been assigned to sample *a* and to a similar crystal mentioned above. The results predict a T_c of 3.8°K for a single NbSe₂ layer. Also shown in Fig. 2 are the results of Gamble *et al.*¹ for the transition temperatures obtained from the onset of superconductivity as measured by susceptibility for bulk NbS₂ intercalated with aniline, giving a layer separation of 18.1 Å, and bulk TaS₂ intercalated with stearamide, giving a layer separation of 57 Å. Our T_c results give support to the suggestion that layers widely separated by intercalation are to a large extent two dimensional. When crystals are intercalated, the width of the transition is observed to increase from less than 0.2°K to 0.5 to 1°K,¹ whereas our results suggest that the transition width for a single layer of NbSe₂ may not differ significantly from the bulk value. The broadened transition may be intrinsic to intercalated materials, as suggested by Di Salvo *et al.*¹⁰

The author would like to thank A. D. Yoffe for his interest in this work and T. H. Geballe for sending us a preprint of work to be published. This work was supported by the National Research Council of Canada.

*Now on leave at the Cavendish Laboratory, Cambridge, England.

¹F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. Di Salvo, and T. H. Geballe, to be published.

²See the review by J. A. Wilson and A. D. Yoffe, *Advan. Phys.* **18**, 193 (1969).

³E. Revolinsky, G. A. Spiering, and D. J. Beernsten, *J. Phys. Chem. Solids* **26**, 1029 (1965).

⁴R. Kershaw, M. Vlasse, and A. Wold, *Inorg. Chem.* **6**, 1599 (1967).

⁵A. J. Grant, D. Jerome, and A. D. Yoffe, to be published.

⁶H. N. S. Lee, H. McKinzie, D. S. Tannhauser, and A. Wold, *J. Appl. Phys.* **40**, 602 (1969).

⁷J. Edwards and R. F. Frindt, *J. Phys. Chem. Solids* **32**, 2217 (1971).

⁸R. F. Frindt, *J. Appl. Phys.* **37**, 1928 (1966).

⁹F. Consadori and R. F. Frindt, *Phys. Rev. B* **2**, 4893 (1970).

¹⁰F. J. Di Salvo, R. Schwall, T. H. Geballe, F. R. Gamble, and J. H. Osiecki, *Phys. Rev. Lett.* **27**, 310 (1971).

Electron-Spectrometric Study of Amorphous Germanium and Silicon in the Two-Phonon Region

Bernd Schröder and Jürgen Geiger

*I. Physikalisches Institut, Technische Universität Berlin, Berlin, Germany, and Fachbereich Physik, Universität Trier-Kaiserslautern, Kaiserslautern, Germany**

(Received 22 November 1971)

The energy-loss spectra of 25-keV electrons transmitted through thin amorphous Ge and Si films have been measured in the range of very small energy losses between 25 and 400 meV. The resolution was 4 and 6 meV. The main intensity in the spectra is located at low energy and is caused by "defect-induced" two phonon excitation.

In a series of former papers^{1,2} monoenergetic fast electrons (25–35 keV primary energy) were shown to interact strongly with optical phonons and surface phonons³ in ionic crystal films. The strength of interaction of fast electrons appeared to be quite similar to that of electromagnetic radiation, which is strongly absorbed by ionic crystals at the frequencies of the transverse optical vibrations because of the large dipole moment connected with the vibrating lattice.

In the present paper the interaction of electrons with thin films of amorphous germanium and silicon is investigated. Since these targets consist of atoms of the same sort, light can couple with lattice vibrations only via transition moments of higher orders, and weak absorption due to two-phonon excitation is observed instead. For example, the maximum absorption coefficient of LiF is⁴ $K = 40\,000\text{ cm}^{-1}$ which is to be compared with $K = 30\text{ cm}^{-1}$ in the two-phonon region of Ge.⁵ Two-phonon excitations by fast electrons, therefore, are expected to be very weak, and energy losses corresponding to these processes would be observed only under great difficulties. Fortunately, as it turned out, these difficulties were not that serious because the intensity of the corresponding energy losses can be enhanced to a certain extent by the distorted structure of the films.

The highly resolved electron energy-loss spectra of Ge and Si (Figs. 1 and 2) were obtained by means of a Wien filter spectrometer.⁶ The energy of the electrons was 25 keV, the energy reso-

lution 4 and 6 meV. The self-supporting films (thickness between 150 and 650 Å) have been prepared by evaporation on to a freshly cleaved NaCl crystal. Electron diffraction shows the amorphous structure of the films. During handling the films were exposed to open air so that some oxidation of the films occurs.

The intensity of the energy losses within the phonon region (indicated in Figs. 1 and 2) depends on the conditions during the preparation of the film, that is on the residual gas pressure and on the rate of evaporation, if the pressure is not too low. The phonon intensity increases with decreasing rate of evaporation and with increasing pressure. The same behavior is found for the electric resistance ρ_s of the films.⁷ One reason for this dependence is that during the evaporation the material is contaminated by residual gas atoms, mainly oxygen. Secondly, the microstructure of the films will depend on the conditions during evaporation, in the sense that the distortion of the Ge tetrahedra, their mutual order, and the density of voids vary. Hence it is concluded that the noticeable increase in intensity of the two-phonon energy losses is due to "defect-induced" two-phonon excitation. This effect is quite analogous to defect-induced one-phonon excitation discussed by Dawber and Elliot.⁸ Accordingly the two-phonon intensity is particularly weak for the films evaporated in ultrahigh vacuum or for heat-treated polycrystalline films. Simultaneously the underlying background continuum indicated in Fig. 1 increases. The posi-