real weak links are asymmetric enough to eliminate the predicted logarithmic vanishing of R at small V for identical superconductors on the two sides of the junction. In any case, the value of the resistance does not appear in our results in any crucial fasion.

It is a pleasure to thank Professor W. W. Webb for suggesting this problem and Professor V. Ambegaokar for reading and commenting on the manuscript. A travel grant from the Wihuri Foundation, Helsinki, is gratefully acknowledged. I wish to acknowledge the financial support of the Advanced Research Projects Agency, through the Materials Science Center, Cornell University.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 3 1 AUGUST 1972

Pressure Effect on Superconducting $NbSe_2$ and NbS_2 †

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(Received 11 February 1972)

The pressure dependence of the superconducting transition temperature T_c has been measured for NbS_2 and $NbSe_2$ in order to determine whether tunneling between laminar layers is a dominant factor controlling T_c. Measurements of the lattice constants by x-ray diffraction indicate that both materials are very compressible along the c axis, but T_c measurements do not correlate with the c-axis lattice constant. $NbSe_2$ shows a rapid change in T_c with pressure, whereas NbS_2 shows practically no change at all. T_c measurements correlate with intralaminar changes much better than they correlate with interlaminar spacings.

INTRODUCTION

Superconductivity in layer-structure compounds has special features associated with the extreme anisotropy of the material.[1-4] For these substances, the chemical binding within the trigonal prismatic laminar plane is very strong and transport properties parallel to the laminar are similar to those of ordinary metals. Transport properties perpendicular to the laminar, however, show a high impedance to particle motion because the chemical binding has a weak van der Waals character. In fact, the coupling between lamina is so weak that one is tempted to think of the 6-Å-thick lamina as independent layers and to discuss the material as though it were a two-dimensional superconductor.[5–7]

Theoretical attempts to describe superconductivity in these compounds generally have focused attention on the need for Josephson tunneling between layers to maintain the phase coherence over large distances.[2,8] Indeed, Katz[4] has suggested that the rapid depression of T_c in $NbSe_2$ with excess Nb[9] can be explained in terms of the change in tunneling between lamina as the excess Nb increases the interlaminar spacing. The addition of excess Nb, of course, could also change T_c via other mechanisms.

In the present work, we have tested the tunneling hypothesis by measuring both the change in T_c and the change in lattice constant as pressure is applied. The compounds $NbSe_2$ and NbS_2 are both soft in the c direction so that a modest pressure of 10 kbar can induce a lattice constant change of 1% or more. Hence one can test the tunneling hypothesis without the complication of additional atoms between the layers as in the intercalation[5–7] and stoichiometry experiments.[9]

EXPERIMENTAL

Samples were produced from the elemental constituents by an iodine-vapor transport method.[10] The transport tube was 5 cm in diameter and the transport distance was about 12 cm. Samples of both materials were obtained in the form of single-crystal plates several mm on a side and up to 1 mm thick. From the value of T_c at zero pressure, it appears that the $NbSe_2$ is very close to the expected stoichiometry.[11]

The pressure dependence of the lattice parameters was determined at room temperature in a beryllium pressure cell described elsewhere.[12] Kerosene was used as a pressure-transmitting fluid and Cu $K\alpha$ x radiation was used in conjunction with counter methods to detect the Bragg peaks. Ten different peaks were used in the determination of the lattice constants at each pressure.

The pressure dependence of T_c was determined by a clamp technique similar to that of Chester and Jones.[13] A beryllium-copper piston and cylinder apparatus, shown in Fig. 1, was used to apply the pressure at room temperature and a clamp was used to retain it after removal from the press. The clamp arrangement was then mounted in a standard chamber for the measurement of T_c using magnetic susceptibility. We found that at 1 : 1 mixture of isoamyl alcohol and n-pentane gave the sharpest superconducting transition, in accordance with previous work by Chu, Smith, and Gardner.[14] Pressures were determined from the superconducting transition of a tin wire mounted below the sample in the bomb.[15] The laminar samples were composed of many small crystals with random orientation.

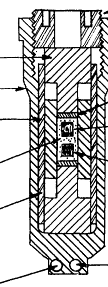

FIG. 1. Clamp arrangement used for the measurement of T_c. The pressure-transmitting fluid was a 1 : 1 mixture of n-pentane and isoamyl alcohol. The Sn manometer was a coil of ribbon about 0.120 in. wide by 0.005 in. thick.

RESULTS AND DISCUSSION

The pressure dependence of the lattice constants, shown in Fig. 2, indicates that both NbS_2 and $NbSe_2$ are indeed soft in the c-axis direction, as expected for van der Waals coupling. For NbS_2 the length of the c axis decreases linearly from 17.918 Å at 1 bar to 17.857 Å at 3.1 kbar, whereas the length of the a axis decreases from 3.3303 to 3.3286 Å in the corresponding pressure interval. These values give 1.6 (±0.4) × 10^{-4} and 11.0 (±0.4) × 10^{-4} $kbar^{-1}$ for K_a and K_c, respectively, where K_a is the linear isothermal compressibility in the basal plane and K_c is the corresponding quantity along the trigonal axis. For $NbSe_2$, the compressibilities are somewhat larger. The c axis contracts from 12.525 to 12.462 Å and the a axis contracts from 3.4403 to 3.4359 Å in the 0–3.1-kbar range, yielding $K_a = 4.1$ (±0.4) × 10^{-4} and $K_c = 16.2$ (±0.5) × 10^{-4} $kbar^{-1}$. In both cases, the lattice constants vary linearly with pressure so that one can extrapolate to 10 kbar with some confidence.

Results for the pressure dependence of the superconducting transitions are shown in Fig. 3. For the case of $NbSe_2$, the data show that the sample is of high quality. The transitions are about 0.060 K wide at all pressures, indicating that the sample is homogeneous and not badly strained when pressure is applied. In addition, the relatively high value of the zero pressure T_c, 7.13 K for the midpoint of the transition, also indicates that the sample is close to stoichiometry in that slight deviations cause a rapid depression of T_c. The values of the lattice constant and T_c at zero pressure are in good agreement with earlier work.[9,11]

The quality of the NbS_2 is not nearly as good as the $NbSe_2$ sample but the results are similar to work reported in the literature.[16] The transition

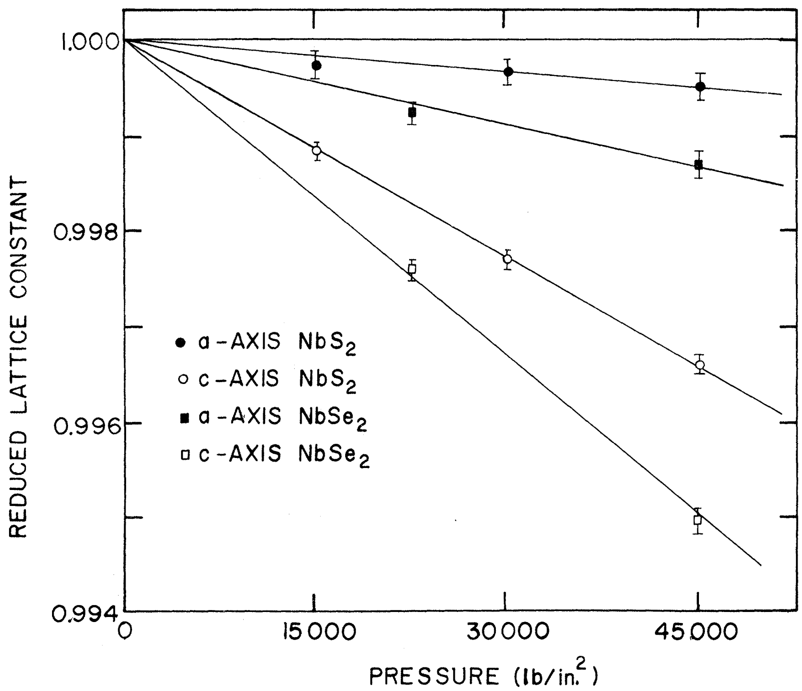

FIG. 2. Pressure dependence of the lattice parameters for NbS_2 and $NbSe_2$.

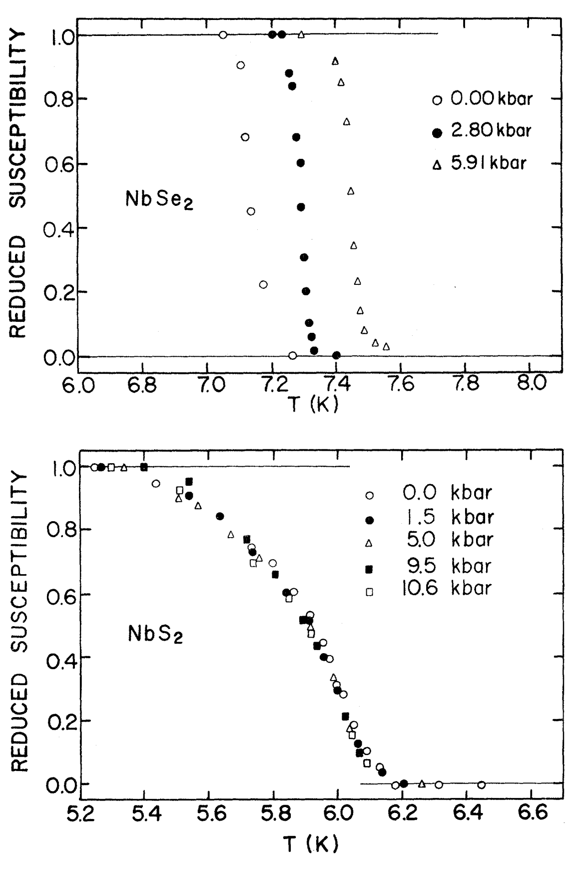

FIG. 3. Superconducting transitions for NbS_2 and $NbSe_2$.

takes place in a range over 0.200 K wide. Fortunately, however, the application of pressure does not change the shape of the transition so that one can meaningfully discuss pressure shifts of any part of the phase transition. From Fig. 3 it is clear that no part of the phase transition shifts by more than 0.050 K with the application of pressure.

Values of T_c defined by the temperature at which the reduced susceptibility goes through 0.5 are plotted in Fig. 4. For $NbSe_2$, T_c rises sharply with pressure in accordance with the recent work of Jerome *et al.*[17] The superconducting transitions reported here occur at somewhat higher temperatures and are somewhat sharper than earlier measurements,[17] but basically the results are the same. The initial low-pressure slope is 5.6×10^{-5} K/bar. For NbS_2, the shift in T_c is less than 0.050 K for 10.6 kbar indicating an initial slope of less than 0.5×10^{-5} K/bar, or at least a factor of 10 smaller than the slope for $NbSe_2$.

It is somewhat surprising to find two materials as apparently similar as NbS_2 and $NbSe_2$ with superconducting pressure effects which differ by a factor of 10. On the basis of earlier theoretical work[2-4] one might expect to observe changes in T_c which correspond to changes in the c-axis lattice constant. However, a 1.1% change in the c axis of $NbSe_2$ changes T_c by more than 0.300 K, whereas a 1.1% change in the c-axis lattice constant of NbS_2 changes T_c by less than 0.050 K. For these materials, the changes in T_c do not

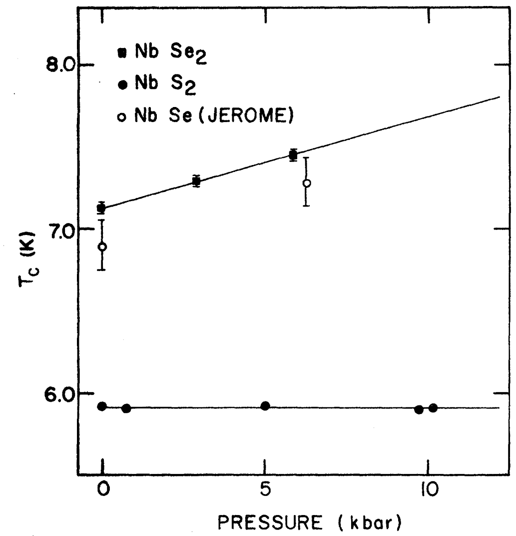

FIG. 4. Pressure dependence of the superconducting transition temperature for NbS_2 and $NbSe_2$.

seem to be controlled by the c-axis spacing. Tunneling between lamina is governed largely by the c-axis spacing, so the data indicate that tunneling is not the dominant ıactor controlling T_c.

The most conspicuous difference between the sulfide and the selenide is in the pressure dependences of the a-axis lattice constant. The a-axis lattice constant of $NbSe_2$ changes about 2.6 times more rapidly with pressure than the corresponding lattice constant for NbS_2 and this means that the area of the unit cell perpendicular to the c axis changes five times as rapidly. The sulfide, which shows a very small change in T_c with pressure, also shows a very small change in the unit-cell area with pressure, whereas the selenide shows a large change in both T_c and the unit-cell area with pressure. Hence the changes in unit-cell area correlate rather well with changes in T_c as the pressure is applied.

SUMMARY

Measurements of the pressure dependence of both the lattice constants and the superconducting transition temperature for NbS_2 and $NbSe_2$ indicate that tunneling between layers is not a dominant factor controlling T_c. The results indicate that intralaminar, rather than the interlaminar, spacings are the important parameter determining T_c.

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†Contribution No. 3203.

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