Superconductivity and Magnetoresistance in $NbSe_2$ †*

R. C. Morris and R. V. Coleman
Department of Physics, University of Virginia, Charlottesville, Virginia 22901

and

Rajendra Bhandari‡
Department of Physics, University of California, Berkeley, California 94720
(Received 2 September 1971)

Electron conduction in single crystals of $NbSe_2$ has been measured at 4.2 °K in magnetic fields up to 150 kOe. The upper critical field H_{c2} has been measured as a function of the angle between the applied field and the layers of the crystal for currents flowing both parallel and perpendicular to the layers. An effective-mass model based on simple considerations of the anisotropy of the crystal has been used to obtain a value for the ratio of effective masses for electron motion parallel and perpendicular to the layers, and the best value obtained is $m_{\parallel}/m_{\perp} = 0.09 \pm 0.01$. Transverse-magnetoresistance rotation diagrams have been studied and structure due to flux flow and flux pinning has been observed.

I. INTRODUCTION

A number of transition-metal dichalcogenides crystallize in layer structures which show metallic behavior over a wide temperature range and become superconducting at low temperatures. A good example of this type of material is $NbSe_2$ which consists of trigonal prismatic Se—Mb—Se sheets with a packing sequence of either two layers (2*H* crystal) or four layers (4*H* crystal) depending on the growth conditions.[1] A discussion of the two crystal structures and of other transition-metal dichalcogenides can be found in the comprehensive review article by Wilson and Yoffe.[2] Both the two- and four-layer phases are superconducting with transition temperatures of 7 and 6.3 °K, respectively.[1,3]

Reported measurements on the resistivity of single crystals of 2*H*-$NbSe_2$ give room-temperature resistivities of 1×10^{-4} to $1.5\times10^{-4}\,\Omega$ cm with a drop in resistivity by a factor greater than 10 between room temperature and 4.2 °K.[4,5] Neither of these sources reports the observation of any anisotropic resistivity behavior. Recently, Edwards and Frindt[6] have carried out a detailed measurement of the conductivity in single crystals and report that the electrical conductivity in the normal phase just above the superconducting transition temperature of 7 °K for 2*H*-$NbSe_2$ shows a ratio $\sigma_{\perp c}/\sigma_{\parallel c} \cong 50$, where *c* is the axis perpendicular to the layers.

Several investigations of the critical current in the superconducting phase[7-9] have shown strong anisotropic behavior in the superconducting characteristics. For example, in low magnetic fields the critical current may be as much as ten times larger for fields parallel to the layers as for fields perpendicular to the layers.

Antonova *et al.*[9] have studied the magnetization curves for fields up to 3 kOe and find that anisotropic behavior also exists in the magnetization with $M_{\perp}/M_{\parallel} = f(H)$, where $f(H) \geq 1$ for $H < 750$ Oe and $f(H) < 1$ for $H > 750$ Oe. They find a large hysteresis in the magnetization curves for both field directions and attribute this to extended defects in the crystals which serve as pinning centers for flux vortices.

Antonova and co-workers[9-11] have also studied the influence of deviations from stoichiometry on the physical properties of $NbSe_2$. From their measurements of variations in the transition temperature with lattice deformation they conclude that the superconductivity is dependent on the perfection of the niobium sublattice. This includes the ordering of the niobium atoms in one layer as well as the ordering among the layers.

To date the investigations of the anisotropic behavior of the superconducting phase of $NbSe_2$ have centered on the behavior at fields below the second critical field H_{c2}. In the present paper we have examined the resistive behavior of single crystals of $NbSe_2$ at 4.2 °K in magnetic fields up to 150 kOe for currents both parallel and perpendicular to the layers. We have studied the critical field H_{c2} by measuring the resistance transition and we develop a physical theory to account for the anisotropic behavior of H_{c2}. We have also examined some other features which appear at fields above 80 kOe.

II. EXPERIMENTAL PROCEDURE

Single crystals of $NbSe_2$ were prepared by the method of iodine-transport reactions according to the procedure of Kershaw *et al.*[4] Crystals usually grew in a thin-sheet form, but a number of growths included crystals with thicknesses of greater than

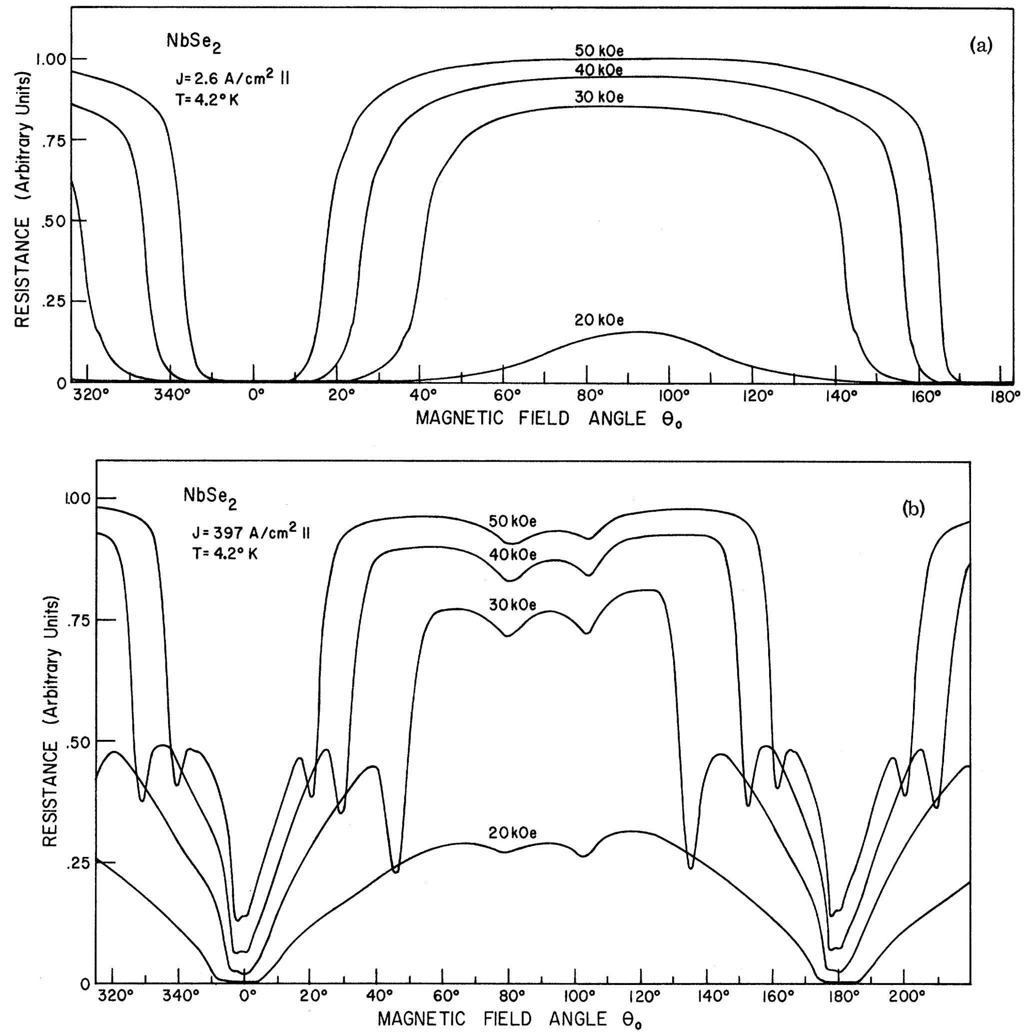

FIG. 1. Resistance vs angle of magnetic field with plane of layers for different values of field. (a) $NbSe_2$ crystal with J parallel to layers. (b) $NbSe_2$ crystal showing deviation from stoichiometry around 90° along with maxima and minima of resistance in the flux-flow region. J parallel to layers.

0.7 mm. Samples were prepared by slicing the crystals into bar-shaped samples with widths of 0.5–1 mm and lengths 5–6 mm. The thickness perpendicular to the layers was in the range 0.15–0.52 mm. Electrical connections were made with indium solder. Resistance measurements were made using the standard four-lead arrangement.

The crystal structure was not analyzed directly, but the method of preparation should ensure the growth of the $2H$-crystal structure.[4,9] For the samples measured, 4.2 °K resistivities ranged from 6×10^{-6} to 16×10^{-6} Ω cm for currents parallel to the layers and approximately 3×10^{-4} Ω cm for currents perpendicular to the layers. Samples with thick c dimensions tended to have higher calculated resistivities, possibly indicating an uneven current distribution in the sample. Room temperature to 4.2 °K resistance ratios for the crystal investigated varied from 20 to 65.

Current densities were kept relatively low for most measurements in order to minimize flux-flow resistance below H_{c2}. Densities on the order of 5 A/cm^2 and less were typical of those used. Higher current densities did not affect H_{c2} but did make it more difficult to determine accurately.

III. MAGNETORESISTANCE MEASUREMENTS

Magnetoresistance rotation diagrams have been recorded for samples with current flowing both parallel and perpendicular to the layers. For fields up to about 80 kOe these rotation diagrams are characterized by a deep minimum for field directions approaching the orientation parallel to the layers ($H_{\parallel}$), while a large dc voltage is observed

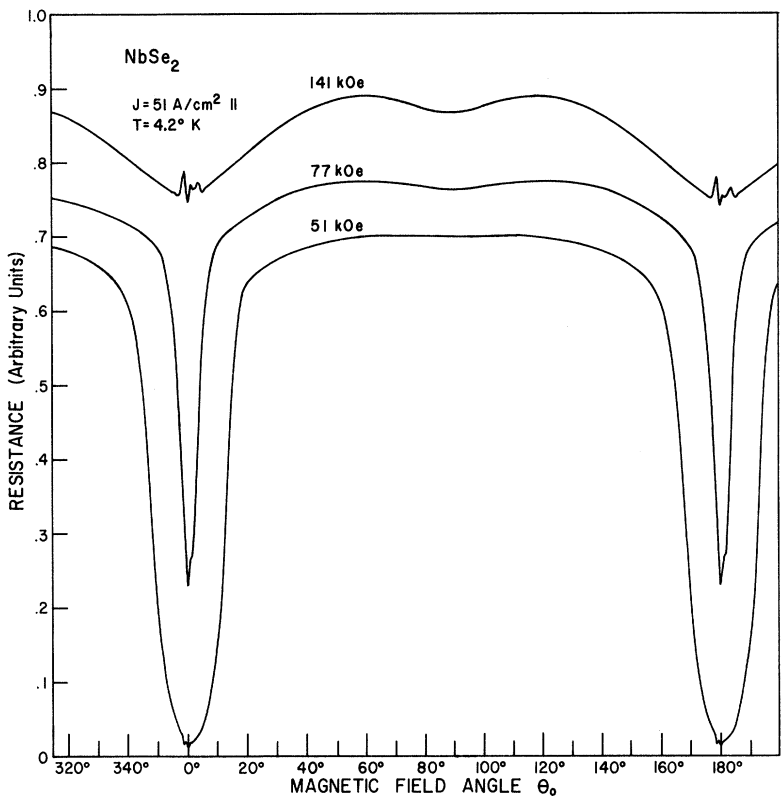

FIG. 2. Resistance vs angle of magnetic field with plane of layers for fields above 50 kOe. J parallel to layers.

for fields approaching the orientation perpendicular to the layers ($H_\perp$). Typical rotation diagrams for J parallel to the layers are shown in Figs. 1(a) and 1(b) for various values of the magnetic field. The rotation curves for J perpendicular to the layers show the same general features and no definite differences are observed in the magnetoresistance behavior for $J_\parallel$ and $J_\perp$. However, structure due to flux flow is observable at lower current densities in the $J_\perp$ case.

At high fields additional aniotropy is observed near the $H_\perp$ orientation and this corresponds to a shallow minimum in the dc resistance, as shown in the upper curve of Fig. 2. As shown in the set of curves in Fig. 1(b) considerable structure is seen in some specimens as the field is rotated away from the $H_\parallel$ position. This corresponds to flux flow in the superconducting phase and the intermediate maxima and minima would appear to occur as a consequence of flux pinning. This phenomenon is not observed in what we believe to be the more perfect specimens as shown in the curves of Fig. 1(a). The details of the flux-flow structure are a sensitive function of the current density and also appear in the field dependence of resistance curves measured for the appropriate field orientations. Structure due to flux flow in $NbSe_2$ has also been observed in measurements of critical currents as a function of field orientation as reported by Spiering *et al.*[8] and by Antonova *et al.*[9] The latter showed that the structure was enhanced in crystals with deviations from perfect stoichiometry.

The deep minimum which is centered on the $H_\parallel$ orientation of the rotation curves is due to the superconducting transition which occurs as H approaches the $H_\parallel$ orientation, and the angular width of this minimum decreases with increase of the magnetic field applied to the sample. This behavior is of course consistent with the expectation that the component of the field perpendicular to the layers plays the dominant role in quenching the superconductivity. As shown in Fig. 2, the minimum becomes narrower and narrower at higher fields until for fields above about 70 kOe the dc resistance begins to increase rapidly for H parallel to the layers. However, sharp structure at the $H_\parallel$ orientation persists up to the highest field of 141 kOe, as shown in the upper curve of Fig. 2.

The field dependence of dc voltage can be used to determine the approximate critical field for various orientations of the field with respect to the layers. Such plots are shown in Fig. 3 for both $H_\parallel$ and $H_\perp$. The critical field for destruction of superconductivity is estimated from the resistive transition and is determined by the construction indicated by the dotted lines in Fig. 3. As can be seen from Fig. 3 the resistive transition becomes considerably wider as the field approaches the $H_\parallel$

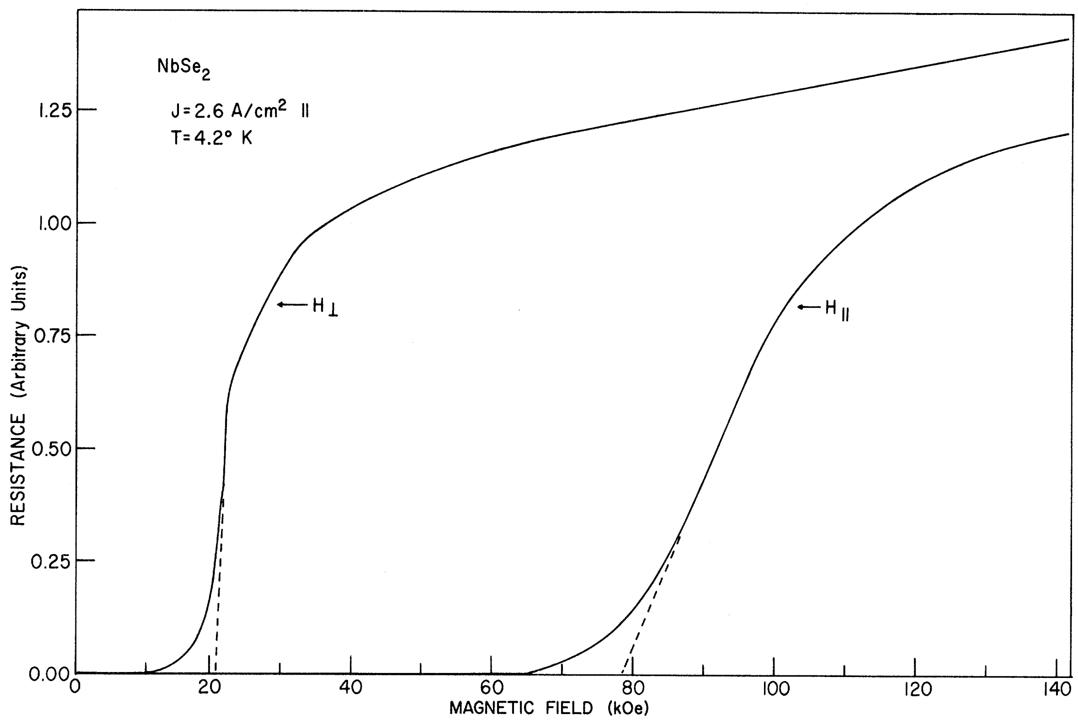

FIG. 3. Resistance vs applied magnetic field for fields parallel and perpendicular to the layers of $NbSe_2$ crystal. J parallel to layers.

orientation. For fields well above the critical field the magnetoresistance approaches a linear dependence on field. A plot of the critical field versus the angle away from the $H_{\parallel}$ orientation is shown in Fig. 4 for J both parallel and perpendicular to the layers. For the $H_{\parallel}$ orientation the critical fields reach approximately 75 and 65 kOe for $J_{\parallel}$ and $J_{\perp}$, respectively. The dependence of the critical field on the angle of the applied field with respect to the layers can be calculated from theoretical considerations and the data are compared to the appropriate expressions in Sec. IV.

IV. DISCUSSION AND CONCLUSIONS

The layered superconductors of which $NbSe_2$ is an example show the general behavior expected for a type-II superconductor with large anisotropies introduced by the anisotropic nature of the crystal structure. The main quantitative feature investigated in the present study is the dependence of the upper critical field H_{c2} on the angle θ_0 which the applied magnetic field makes with the layers. We shall derive from very simple considerations an expression for the upper critical field of a layered superconductor and compare the experimental results with this expression. The model is based on an effective-mass approximation and allows us to determine from the experimental data the ratio of the effective masses for motion of electrons parallel and perpendicular to the layers.

In the isotropic case, the upper critical field at 0 °K is given by

$$H_{c2}=\phi_0/2\pi\xi^2\,, \tag{1}$$

where $\phi_0=hc/2e$ is the flux associated with a fluxoid and ξ is the coherence length, representing the scale of variation of the wave function ψ in the material, and is the same in all directions in an isotropic material. In a layered superconductor, since the overlap of electron wave functions is larger within the layers than between layers, it is natural to assume that the electrons have a high effective mass for motion normal to the layers and a low effective mass for motion within a layer. Let the z axis be normal to the layers so that the mass tensor has the form

$$m_{ij}=\begin{pmatrix} m & 0 & 0\\ 0 & m & 0\\ 0 & 0 & M\end{pmatrix}\,, \tag{2}$$

where $M>m$.

Since the coherence length ξ depends on the effective mass[12] as

$$\xi \propto 1/m^{1/2}\,, \tag{3}$$

the coherence length also becomes a tensor and is given by

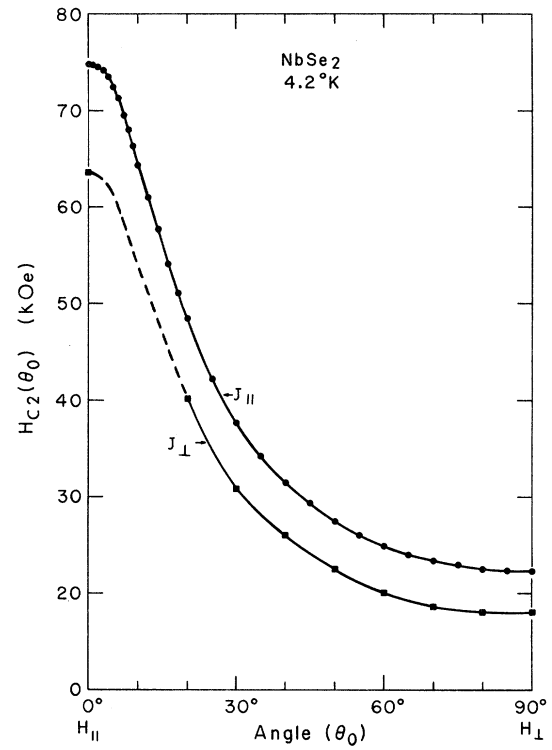

FIG. 4. Upper critical field H_{c2} vs angle of magnetic field with a plane of layers for J parallel to layers and J perpendicular to layers, $T=4.2\,°K$.

$$\xi_{ij}=\begin{pmatrix}\xi & 0 & 0\\ 0 & \xi & 0\\ 0 & 0 & \epsilon\xi\end{pmatrix}, \tag{4}$$

where

$$\epsilon=(m/M)^{1/2}. \tag{5}$$

Now in order to find the upper critical field of the layered solid when the magnetic field makes an angle θ_0 with the plane of the layers, assuming that the material remains type II for all orientations, we modify (1) by replacing the area $\pi\xi^2$ of a circular fluxoid by an area $\pi\xi_a\xi_b$. This is the cross-sectional area of an elliptical fluxoid which will be formed in this case with its cross section in a plane perpendicular to the magnetic field. ξ_a and ξ_b are the two principal coherence lengths in this plane. We therefore have

$$H_{c2}=\phi_0/2\pi\xi_a\xi_b. \tag{6}$$

The cases when $\theta_0=0°$ and $\theta_0=90°$ have been dealt with by Lawrence and Doniach.[13]

Since the maximum coherence length ξ is in the plane of the layers, i.e., the xy plane, one of the two principal directions will be the line of intersection of the plane normal to the magnetic field with the xy plane. Let us call this the x direction. Hence one of the two principal coherence lengths is ξ.

Let

$$\xi_a=\xi\,; \tag{7}$$

now the coherence length in any direction in the solid will be given by the length of the vector joining the center of the ellipsoid given by Eqs. (8) to the surface of the ellipsoid in that direction:

$$x=\xi\,\sin\theta\,\cos\phi\,,$$
$$y=\xi\,\sin\theta\,\cos\phi\,, \tag{8}$$
$$z=\epsilon\xi\,\cos\theta\,.$$

The second principal length ξ_b, which is in a direction normal to the x axis and in the plane normal to H, is therefore given by the length of the vector $(0,\ \xi\,\sin\theta_0,\ \epsilon\xi\,\cos\theta_0)$. ($\theta_0$ is the angle between H and the plane of the layers.)

Hence we have

$$\xi_b=\xi\,(\sin^2\theta_0,\ +\epsilon^2\cos^2\theta_0)^{1/2}. \tag{9}$$

Therefore, from (6), (7), and (9), we have

$$H_{c2}(\theta_0)=\frac{\phi_0}{2\pi\xi^2\,(\sin^2\theta_0+\epsilon^2\cos^2\theta_0)^{1/2}} \tag{10}$$

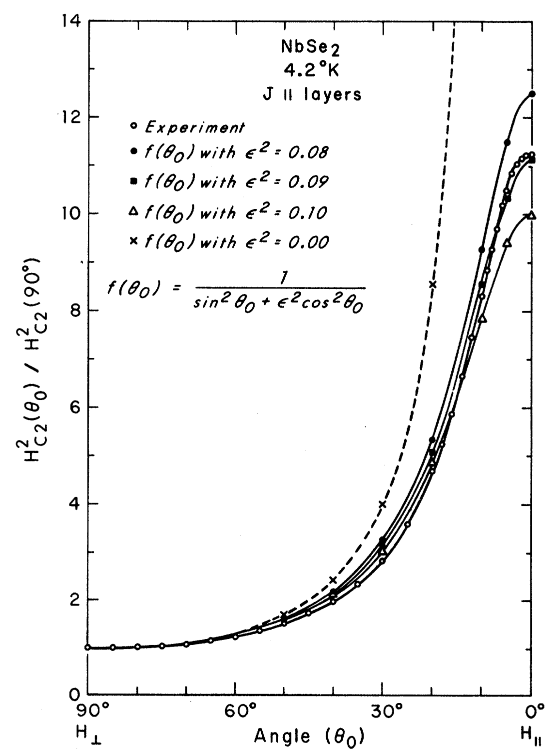

FIG. 5. Experimental curve of $H^2_{c2}(\theta_0)/H^2_{c2}(90°)$ vs angle θ_0 of magnetic field with plane of layers for $NbSe_2$ crystal with J parallel to layers. Theoretical curves of $f(\theta_0) = (\sin^2\theta_0+\epsilon^2\cos^2\theta_0)^{-1}$ for four values of ϵ^2 are also shown.

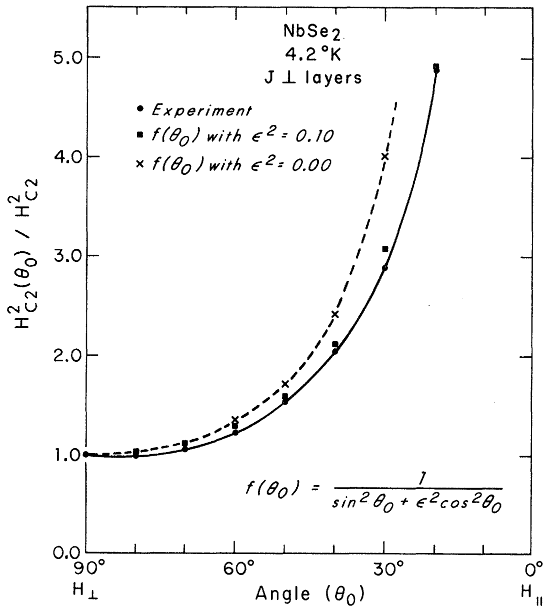

FIG. 6. Experimental curve of $H^2_{c2}(\theta_0)/H^2_{c2}(90°)$ vs angle θ_0 of magnetic field with plane of layers for NbSe$_2$ crystal with J perpendicular to layers. Theoretical curves of $f(\theta_0) = (\sin^2\theta_0 + \epsilon^2\cos^2\theta_0)^{-1}$ for $\epsilon^2 = 0$ and $\epsilon^2 = 0.10$ are also shown.

or

$$H_{c2}(\theta_0) = \frac{H_{c2\perp}}{(\sin^2\theta_0 + \epsilon^2\cos^2\theta_0)^{1/2}} , \qquad (11)$$

where

$$H_{c2\perp} = \phi_0/2\pi\xi^2 \qquad (12)$$

is the upper critical field normal to the layers and $\epsilon^2 = m/M$. The angular dependence given by (11) is essentially the same as that arrived at by Katz[14,15] by a more sophisticated approach.

We have fit the experimentally measured curves for $H_{c2}(\theta_0)/H_{c2\perp}$ to the function of θ_0 given by (11), using ϵ as an adjustable parameter. As can be seen from Figs. 5 and 6 it is possible to get a reasonably good fit by varying only the one parameter. Figure 5 shows experimental data for a typical sample with J parallel to the layers. Theoretical curves for various values of the parameter ϵ^2 are also shown in order to give an idea of the sensitivity of the fit. The best value of $\epsilon^2 = m/M$ is determined to be 0.09 ± 0.01. Figure 6 shows similar data for a sample with J perpendicular to the layers and the best value of ϵ^2 is estimated to be 0.10 for this data. A number of other specimens have also been compared to $f(\theta_0)$ and give values in the neighborhood of 0.10, although we have observed some variation from specimen to specimen with the highest observed value of ϵ^2 being 0.15.

For the present experiments on pure NbSe$_2$ the model appears to fit the data fairly well and is probably an adequate model of the behavior. However, as pointed out by Lawrence and Doniach[13] such an effective-mass description may break down if the coherence length perpendicular to the layers becomes too small, as might be the case in the intercalated layer compounds[16–18] where the layers are spread much further apart than in the pure material. It should be quite interesting to obtain similar data on the intercalated compounds.

ACKNOWLEDGMENTS

The authors would like to thank Professor Leo Falicov for many stimulating discussions and continued interest in the work. C. E. T. Goncalves da Silva has also contributed substantial to the discussions. Professor D. Sellmyer has made major contributions to the work at the National Magnet Laboratory. Phillip Sommer and Werner Frewer have constructed important parts of the apparatus.

†Work supported by ONR under Contract No. N000-14-69-A-0429.

*Work above 80 kOe was performed while the authors were Guest Scientists at the Francis Bitter National Magnet Laboratory, which is supported at M.I.T. by the National Science Foundation.

‡Work supported by National Science Foundation under Contract No. NSF-GP-13889.

[1]E. Revolinsky, G. A. Spiering, and D. J. Beerntsen, J. Phys. Chem. Solids 26, 1029 (1965).

[2]J. A. Wilson and A. D. Yoffe, Advan. Phys. 18, 193 (1969).

[3]E. Revolinsky, E. P. Lautenschlager, and C. H. Armitage, Solid State Commun. 1, 59 (1963).

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

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

[6]J. Edwards and R. F. Frindt, J. Phys. Chem. Solids 32, 2217 (1971).

[7]D. J. Beerntsen, G. A. Spiering, and C. H. Armitage, IEEE Trans. Aerospace 2, 816 (1964).

[8]G. A. Spiering, E. Revolinsky, and D. J. Beerntsen, J. Phys. Chem. Solids 27, (1966).

[9]E. A. Antonova, S. A. Medvedev, and I. Yu. Shebalin, Zh. Eksperim. i Teor. Fiz. 57, 329 (1969) [Sov. Phys. JETP 30, 181 (1970)].

[10]E. A. Antonova, K. V. Kiseleva, and S. A. Medvedev, Fiz. Metal. i Metalloved. 27, 441 (1969) [Phys. Metals Metallog. (USSR) 27, 58 (1969)].

[11]E. A. Antonova, K. V. Kiseleva, and S. A. Medvedev, Zh. Eksperim. i Teor. Fiz. 59, 54 (1970) [Sov. Phys. JETP 32, 31 (1971)].

[12]Alexander L. Fetter and Pierre C. Hohenberg, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), p. 821.

[13]W. E. Lawrence and S. Doniach, in *Proceedings of the International Conference on Low Temperature Physics.*

1970 (Academic Press of Japan, Tokyo, 1970), Vol. 12, p. 361.

[14]E. I. Katz, Zh. Eksperim. i Teor. Fiz. 56, 1675 (1969) [Sov. Phys. JETP 29, 897 (1969)].

[15]E. I. Katz, Zh. Eksperim. i Teor. Fiz. 58, 1471 (1970) [Sov. Phys. JETP 31, 787 (1970)].

[16]F. R. Gamble, F. J. Di Salva, R. A. Klemm, and T. H. Geballe, Science 168, 568 (1970).

[17]F. J. Di Salva, R. Schwall, T. H. Geballe, F. R. Gamble, and J. H. Osiecki, Phys. Rev. Letters 27, 310 (1971).

[18]T. H. Geballe, A. Menth, F. J. Di Salva, and F. R. Gamble, Phys. Rev. Letters 27, 314 (1971).

PHYSICAL REVIEW B VOLUME 5, NUMBER 3 1 FEBRUARY 1972

Occurrence of Superconductivity in Simple-Cubic $(Au_{1-x}Pd_x)Te_2$ Alloys

Wilkie Y. K. Chen and C. C. Tsuei
W. M. Keck Laboratory of Engineering Materials,
California Institute of Technology, Pasadena, California 91109

(Received 23 September 1971)

The superconducting transition temperatures and lattice parameters of metastable simple-cubic alloys $(Au_{1-x}Pd_x)Te_2$, with $0 \leq x \leq 0.6$, obtained by rapid quenching from liquid state, have been measured as a function of x. As x increases the transition temperature T_c goes through a minimum of 1.6 °K near $x = 0.05$, and then increases steadily to a maximum of 4.5 °K at $x = 0.45$. The lattice parameter shows a slight linear decrease as x increases. The transverse magnetoresistance for the composition $x = 0.2$ saturates at a relatively low field (~2 kG) and is unusually large (~0.14). The initial depression of T_c with increasing Pd content can be interpreted in terms of the information obtained in a previous study of binary Au-Te alloys. The unusual increase of T_c with further increase in the Pd concentration is not well understood.

I. INTRODUCTION

Superconductivity in metastable simple-cubic alloys (with one atom per unit cell) has been reported previously.[1-5] It was also pointed out that all the simple-cubic alloy phases found so far are superconductors with transition temperatures ranging from approximately 1 to 7 °K.[4] These findings suggest that this rather unusual crystal structure is favorable for the occurrence of superconductivity. Among the simple-cubic alloys, the Au-Te system has been studied in some detail.[5,6] It has been shown that the anomalies in the variation of lattice parameter, thermoelectric power, and superconducting transition temperature (T_c) with concentration in this alloy system can be qualitatively explained in terms of a Fermi-surface–Brillouin-zone interaction. A study of the effect of magnetic-impurity atoms such as Mn and Fe on the lattice parameter and on the superconducting transition temperature of the Au-Te alloys has been published.[6] The results of this study give additional support to the electronic band structure proposed for the simple-cubic Au-Te alloys.[5] Furthermore, the results also show that the addition of Fe or Mn monotonically decreases the superconducting transition temperature. The rate of depression of T_c by Fe, however, is about seven times smaller than that by Mn. This is consistent with the fact that Mn carries a localized magnetic moment in the Au-Te alloys while Fe does not.

A preliminary study has shown that Pd can be substituted for Au in $AuTe_2$ alloys, and these alloys are superconducting.[4] In view of the fact that the element Pd is nearly ferromagnetic it seems to be worthwhile to study the compositional dependence of T_c and the lattice parameter as the Au in $AuTe_2$ is replaced by Pd.

II. EXPERIMENTAL PROCEDURE

The compositions of the alloys investigated are of the form $(Au_{1-x}Pd_x)Te_2$, where $0 \leq x \leq 0.6$. The alloys were prepared by induction melting of the appropriate quantities of the constituents (99.999% pure Te and 99.99% pure Au, Pd) in quartz crucibles under an argon atmosphere. The weight losses were found to be less than 0.2% so the nominal compositions of the alloys were taken as the actual ones. The simple-cubic phase was obtained by liquid quenching at a rate of about 10^7 °C/sec, using the "gun" technique.[7] The structure of each quenched specimen was checked by taking diffraction patterns with a Norelco x-ray diffractometer (Cu $K\alpha$ radiation). The lattice parameters of the simple-cubic phase were obtained from Debye-Scherrer films using the Nelson-Riley extrapolation function. The results of the lattice-parameter measurements are shown in Fig. 1. It was found that it became increasingly difficult to obtain a single phase for alloys with x approaching 0.5. In the x-ray dif-