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A. Briggs, P. Monceau, M. Nunez-Regueiro, M. Ribault, J. Richard. Superconductivity of NbSe<sub>3</sub>. Journal de Physique, 1981, 42 (10), pp.1453-1459. 10.1051/jphys:0198100420100145300 . jpa-00209337

**HAL Id: jpa-00209337**

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Submitted on 4 Feb 2008

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Classification

Physics Abstracts

62.50 — 74.10 — 74.60

## Superconductivity of NbSe<sub>3</sub>

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(Reçu le 6 février 1981, révisé le 18 mai, accepté le 10 juin 1981)

**Résumé.** — Nous avons mesuré les transitions résistives supraconductrices de NbSe<sub>3</sub> sous champ magnétique pour des pressions supérieures à celles nécessaires à la suppression de l'onde de densité de charge qui apparaît à 59 K à pression ambiante. NbSe<sub>3</sub> est alors un supraconducteur massif anisotrope avec un effet Meissner total. Les anisotropies des champs magnétiques critiques sont bien décrites par un modèle de masses effectives qui sont en bon accord avec celles déduites des mesures de conductivité ou des mesures d'oscillations Shubnikov-de Haas. A pression ambiante, nous avons mesuré des transitions avec résistivité nulle pour des échantillons de NbSe<sub>3</sub> compactés mais sans effet Meissner total. Cette supraconductivité n'est pas massive et est due vraisemblablement aux barrières entre les domaines formant le cristal.

**Abstract.** — We report measurements of the resistive superconducting transitions of NbSe<sub>3</sub> as a function of magnetic field for sufficient pressures to destroy the lower CDW. These indicate that NbSe<sub>3</sub> is a bulk anisotropic superconductor with a total Meissner effect. The critical field anisotropies are well described by an effective mass model and the values obtained are in good agreement with those obtained by conductivity or Shubnikov-de Haas measurements. At ambient pressure we have measured zero-resistivity transitions for compacted samples, but do not find a total Meissner effect. Hence this superconductivity is not a bulk effect but is probably associated with barriers between domains in the sample.

**Introduction.** — Among the family of metal-transition trichalcogenides intensively studied these last years, only TaSe<sub>3</sub> and NbSe<sub>3</sub> [1] remain metallic at helium temperature [2, 3]. TaSe<sub>3</sub> has a superconducting transition at 2.2 K [4]. NbSe<sub>3</sub> undergoes two independent charge-density wave transitions with associated lattice distortions at 145 K ( $T_1$ ) and 59 K ( $T_2$ ) [2, 5]. Two other resistive anomalies have been observed : the resistivity drops between 2.2 K and 1.5 K and it is constant down to 0.4 K where it decreases again. But down to 7 mK no zero-resistivity has been measured. Magnetization measurements indicate that a very small part of the NbSe<sub>3</sub> sample becomes diamagnetic below 2.2 K where the resistivity drops [3]. A filamentary model of superconductivity has been proposed to explain this low temperature behaviour [6]. Under pressure the CDW transition temperatures decrease. It has been shown that  $dT_2/dP = -6.25$  K/kbar [7]. For this pressure and above NbSe<sub>3</sub> is a bulk superconductor with a complete Meissner effect. Zero-resistivity has been measured on doped NbSe<sub>3</sub> samples with impurities of tantalum [8], titanium [9] or zirconium [10], for tempe-

ratures around 1.5 K but no magnetization on these doped samples have yet been reported. We have observed that a zero-resistivity transition occurs in compacted pure NbSe<sub>3</sub> samples. The critical temperature is around 0.9 K.

Hereafter we first review the resistive and magnetic measurements on pure NbSe<sub>3</sub> filaments. Then we describe the experiments on compacted NbSe<sub>3</sub> samples with different size grains. Finally we report measurements on some NbSe<sub>3</sub> monocrystals under pressure. We have determined the critical magnetic fields parallel and perpendicular to the chain direction. NbSe<sub>3</sub> under pressure is an anisotropic superconductor which near  $T_c$  can be described with an effective mass model. The effective masses deduced from the critical magnetic fields for the different crystallographic orientations are in good agreement with those obtained by conductivity and Shubnikov-de Haas measurements.

1. **Pure NbSe<sub>3</sub>.** — The drop in resistivity below 2.2 K is sample dependent [3]. This drop can be a few percent of the resistivity above 2.5 K but we have measured 80% on a bundle of filaments. Fleming does not observe such a drop on very pure samples with resistance ratios of 200 [11]. Below 2.2 K the

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resistivity is strongly dependent on the current density and the critical current decreases exponentially with temperature. The transition can be suppressed with current densities higher than  $1 \text{ A/cm}^2$ . Previous d.c. initial susceptibility measurements on a  $\text{NbSe}_3$  sample of 300 mg at 50 mK in a magnetic field of 1 Oe indicated that less than  $10^{-3}$  of the volume could be superconducting [3]. More accurate magnetization measurements using SQUID magnetometers have been recently reported [12]. On  $\text{NbSe}_3$  samples loosely assembled Buhrman *et al.* show that a small diamagnetic contribution appears around 2 K where the resistivity drops and that at the lowest temperature (a few tens of mK) the diamagnetic signal is 1% of  $-V/4\pi$  in agreement with the limit of our previous measurements. They described a model where individual planes become superconducting around 2 K. At lower temperature the coupling between planes would increase leading to a 2D-3D superconducting transition.

The temperature dependence of the superconducting critical current and the absence of a total Meissner effect exclude a bulk superconductivity and we proposed a filamentary model for the superconducting transition at 2.2 K [6]. However  $\text{NbSe}_3$  is very different morphologically from, for instance  $(\text{SN})_x$ . This polymer is an assembly of fibers of around 100 Å diameter which dominate the superconducting properties [13]. Very recently Fung and Steeds [14] have observed that the CDW lattice consisted of elongated domains with a typical size of  $2 \mu \times 200 \text{ Å} \times 200 \text{ Å}$  for a pure  $\text{NbSe}_3$  sample. Taking into account this observation we have assumed that the CDW order parameter is zero inside the borders between two domains in which the phase of the CDW is constant [15]. At low temperature these borders become superconducting which lead to a multiconnex superconductivity. This assumption can account for the sample dependent behaviour because of the different repartition of domains in different samples.

**2. Compacted  $\text{NbSe}_3$ .** — In compounds like  $\text{NbSe}_3$  where the easy path for electrons is along the chains, the effect of impurities consists of breaking chains; consequently the transport properties are principally due to these interrupted strands. The resistivity measurements between 300 K and 4.2 K that we have made on samples doped with titanium, zirconium, tantalum or after electron irradiation [16] show a strong increase of the resistivity at low temperature. The same behaviour has been observed with proton irradiation [9]. Another method of « dirtying » the samples is to use powders with different grain sizes. We have crushed  $\text{NbSe}_3$  filaments to obtain powder. This powder was passed through several sieves with grain size less than  $100 \mu$  (sample F6) and with grain size between  $43 \mu$  and  $60 \mu$  (sample F8). The compaction of the powder was done under an hydraulic press at 100 bars at room temperature. The sample dimen-

sions are typically  $10 \times 1.5 \times 1 \text{ mm}^3$ . The d.c. resistance is measured by a classical four lead contacts. The current density is typically  $2 \times 10^{-2} \text{ A/cm}^2$ . The insert of figure 1 shows the resistivity variation between 300 K and 4.2 K [17]. The resistivity variation can be separated in two parts : a semiconducting-like variation all the more important as the grain size is smaller and the resistivity variation of the pure  $\text{NbSe}_3$ . The resistivities at 4.2 K normalized to the room temperature resistivity are respectively 2.07 for F6 and 3.54 for F8. It can be seen that anomalies due to the two CDWs at 145 K and 59 K remain which ensures that, although no X-rays determination have been performed on the powder, we measure the real  $\text{NbSe}_3$  phase.

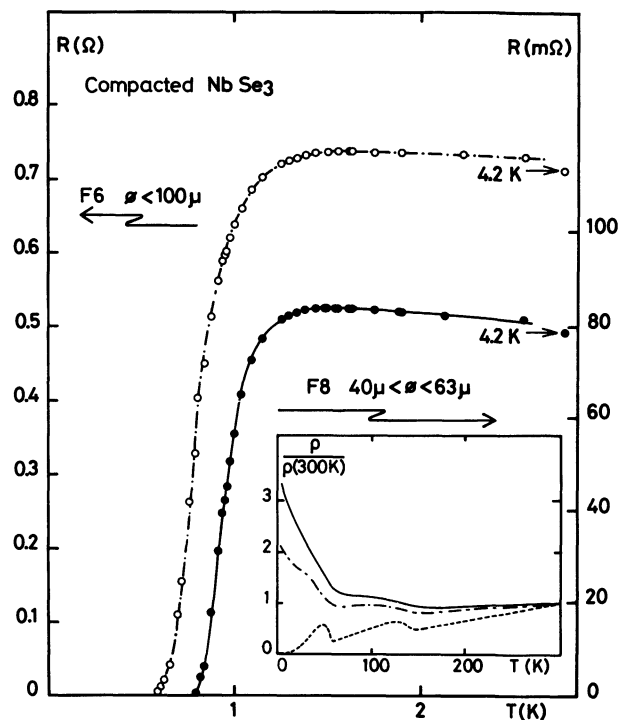


Fig. 1. — Low temperature resistance of compacted powder of  $\text{NbSe}_3$ . The grain size of sample F6 is less than  $100 \mu$  and for sample F8 between  $40 \mu$  and  $63 \mu$ . In the insert, the resistance variation normalized to room temperature as a function of temperature for F6, F8 and a monocystal of  $\text{NbSe}_3$ .

Around 2 K the resistivity saturates. We have measured the resistivity of F6 and F8 in a  $^3\text{He}$  refrigerator. The resistivity variation is shown in figure 1. The resistivity drops to zero for the two samples. If we define the critical temperature at the middle of the transition,  $T_c$  is 0.8 K for F6 and 0.9 K for F8. Initial susceptibility measurements made on F6 show a small diamagnetism of the order of 6% down to 200 mK and increase of this diamagnetism around 100 mK up to 25% of the total diamagnetism.

In figure 2 we show the variation of the resistivity of F6 as a function of magnetic field at different temperatures. Due to the random orientation of each

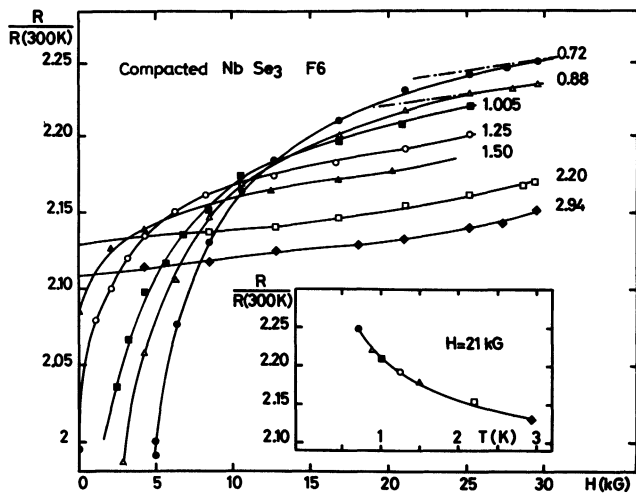


Fig. 2. — Variation of the resistance of F6 normalized to its room temperature resistance as a function of magnetic field at different temperatures. In the insert the normalized resistance at 21 kG as a function of temperature. The resistance increases monotonically when the superconducting state is suppressed by the magnetic field.

grain and the anisotropy of the crystal, the critical fields are not very well defined. But at sufficiently high magnetic fields it can be seen that the magneto-resistance follows the same variation which is the normal state one. We can obtain the resistivity in a fixed magnetic field (21 kG) where the sample is in the normal state (except for the two lowest temperatures where the values are obtained by extrapolation). The insert of figure 2 indicates that when the superconducting state is suppressed (by the magnetic field) the normal resistivity increases monotonically below 2 K.

Our compacted samples are pure NbSe<sub>3</sub> but disordered in the sense that many barriers have been introduced. Although the two CDWs are present, a zero-resistivity is observed below 0.9 K without a complete Meissner effect. To ascertain that zero-resistivity was not a surface property of the compacted sample we cut F6 longitudinally in three parts and we remeasured separately these three parts. No difference in behaviour from the original specimen was observed.

Zero resistivity has also been measured on doped NbSe<sub>3</sub> samples. The resistivity below 2.5 K is current dependent for samples doped with 0.1 % of titanium [9] and with zirconium [10] although the effect of current is less important than for pure NbSe<sub>3</sub> [3]. A superconductivity transition was reported for a NbSe<sub>3</sub> with 5 % of tantalum at 1.5 K [8]. It was stated that the superconductivity arose because the lower CDW was smeared out as similar to the pressure effect. If this is true, as in the case of pressure, a complete Meissner effect must be observed. However no magnetization measurements have yet been performed on doped samples.

Lee and Rice [18] have calculated that the size of the domains where the phase of the CDW is constant decreases with the amount of impurities. So in the

doped samples as in our compacted samples we expect that there is a great number of normal barriers around CDW domains and therefore a superconducting percolation path at low temperature leading to a zero-resistance. However there is not a total Meissner effect.

**3. NbSe<sub>3</sub> under pressure.** — We have measured the resistivity of two single crystals of NbSe<sub>3</sub> under pressure below 4.2 K. The typical dimensions were 5 × 0.02 × 0.005 mm. Precession photographs taken with filtered MoK radiation ensured that the crystals were single crystals with the plane (b, c) in the plane of the ribbon. The crystals were mounted on an araldic disc in a beryllium-copper chester clamp capable of retaining pressures up to 11 kbar at 300 K resulting in about 7.5 kbar at 4.2 K. Pressures were measured at room temperature and nitrogen temperature with a pressure cycled manganin resistance placed near the specimen using the calibration data of Itskevich [19]. For a fixed room temperature pressure, the manganin gauge gave a reproducible nitrogen temperature resistance. The fluid used was an isopentane-methyl 2-pentane mixture. The samples were those used for Shubnikov-de Haas oscillations measurements that we reported previously [7]. For such measurements only two probes on the crystals were necessary which excluded absolute d.c. resistance measurements.

NbSe<sub>3</sub> becomes superconducting when the lower CDW transition is totally suppressed by pressure. In the insert of figure 3 we show the pressure dependence of the CDW transition  $T_2$  and the resistive superconducting transition. Above 5.5 kbar, NbSe<sub>3</sub> is superconducting with a sharp transition and  $T_c$  decreases when the pressure is increased. In the critical pressure range where  $T_2$  varies sharply with pressure,  $T_c$  decreases rapidly and a superconducting transition cannot be detected below 5 kbar. The continuous variation of the resistance for pressures in this range could be due to pressure inhomogeneities. More hydrostatic measurements with helium gas are underway to study this possible coexistence between superconductivity and CDW state.

Figure 3 shows the resistive transitions for pressures of 5.5 kbar and 7.2 kbar. At 7.2 kbar, NbSe<sub>3</sub> undergoes a very sharp superconducting transition at 3.4 K with a width of 0.1 K. The residual resistance of 4 Ω is the contact resistance because of the two probes measurement which varies between 3.2-4 Ω for the different pressures. At 5.5 kbar there is a break in the resistance variation at 3.5 K followed by a continuous decrease of the resistance down to 1.5 K. But if we extrapolate the variation of the magnetic critical fields at  $H = 0$  as we report below, we find a critical temperature of  $3.5 \pm 0.1$  K. Unfortunately because of the two contacts measurements we were unable to measure at ambient pressure the drop in resistivity at 2.2 K.

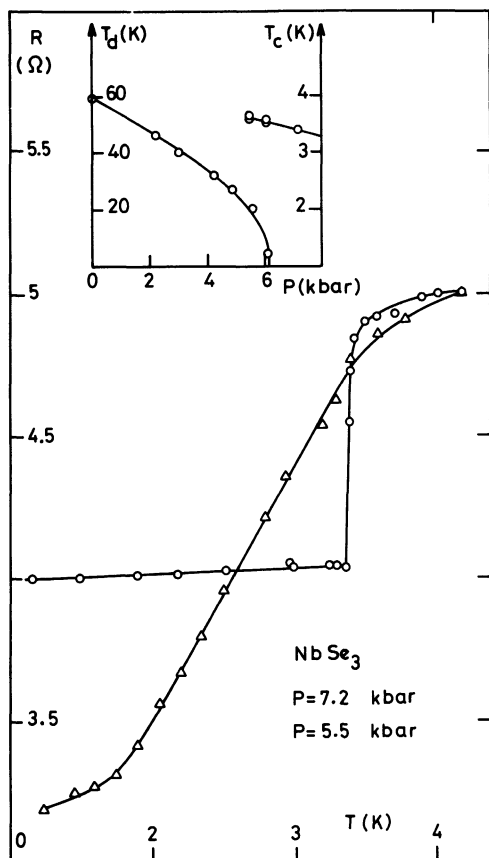


Fig. 3. — Resistive transitions of a monocystal of  $\text{NbSe}_3$  for pressures of 5.5 and 7.2 kbar. The measurements were made with two probes and the residual 3-4  $\Omega$  is the contact resistance. In the insert the variation of the lower CDW transition and the superconducting transition as a function of pressure. When the CDW is suppressed  $\text{NbSe}_3$  becomes a bulk superconductor.

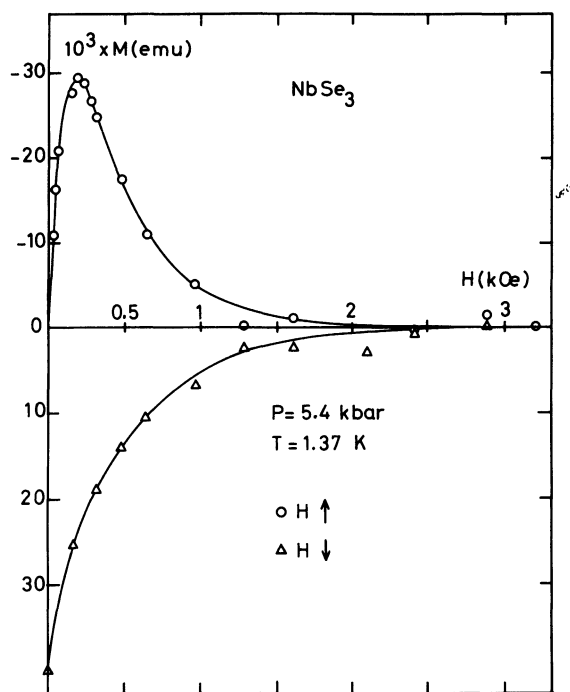


Fig. 4. — Magnetization of a  $\text{NbSe}_3$  sample formed with many fibers at 5.4 kbar and 1.37 K.

We have previously reported initial susceptibility measurements of a specimen consisting of many fibers (specimen C weight of 0.56 g in reference [7]) under pressure. The specimen showed a complete Meissner effect above 5 kbar at 2.5 K. The difference between the superconducting critical temperatures obtained by resistive and magnetic measurements is not well understood and we are trying to clarify this point. Figure 4 shows the magnetization of sample C at 1.37 K for a pressure of 5.4 kbar. This magnetization variation is typical of a superconductor with strong flux trapping.

For magnetic measurements we need to know the angular orientations. The sample has the chains parallel to  $b$  and its large face is parallel to  $(b, c)$ . For the transverse orientation ( $\mathbf{H} \perp \mathbf{b}$ ) we define the azimuthal angle  $\varphi$  between  $\mathbf{H}$  and  $\mathbf{c}$ :  $\varphi = 0$  corresponds to  $\mathbf{H}$  parallel to  $\mathbf{c}$  and  $\varphi = \pi/2$  at  $\mathbf{H}$  parallel at  $\mathbf{a}^*$  (which is different from  $\mathbf{a}$  for the monoclinic structure). The polar angle  $\theta$  is defined in the plane  $(\mathbf{a}^*, \mathbf{b})$  and  $\theta = 0$  corresponds to  $\mathbf{H} \parallel \mathbf{b}$ . The resistive transitions in magnetic fields were performed in two different configurations: firstly with  $\theta = \pi/2$  and  $\varphi = 0$  at 7.7 kbar, for one sample only, in the course of our Shubnikov-de Haas oscillations measurements [7] and secondly at 5.5 and 7.4 kbar with the pressure cell inserted in an electromagnet capable of rotating between  $\theta = 0$  and  $\theta = \pi/2$  with  $\varphi = \pi/2$ , for the two samples. We have drawn in figure 5 typical resistive transitions as a function of magnetic field at the pressures of 5.5 and 7.4 kbar for the orientations  $\varphi = \pi/2, \theta = 0$  and  $\varphi = \pi/2, \theta = \pi/2$ . In figure 6 we have drawn the temperature variation of the critical fields for the three orientations investigated for the same sample. The extrapolation of  $H_{\perp}$  ( $\theta = \pi/2, \varphi = 0$ ) at 7.7 kbar gives  $T_c = 3.25$  K compared to  $T_c = 3.4$  K at 7.4 kbar and 3.5 K at 5.5 kbar. This result confirms the decrease of the critical temperature for pressures greater than those necessary for suppressing the lower

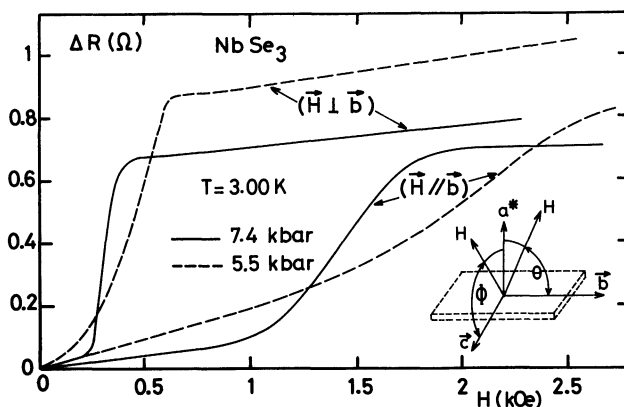


Fig. 5. — Resistive transitions of a monocystal of  $\text{NbSe}_3$  for pressures of 5.5 and 7.4 kbar as a function of magnetic field. The orientation of the magnetic field with the crystallographic axis are shown on the insert.  $\varphi$  is the azimuthal angle with  $H$  in the plane perpendicular to the chain or  $\mathbf{b}$  axis,  $\theta$  is the polar angle with  $H$  rotating in the plane  $(\mathbf{a}, \mathbf{b})$ . The resistive transitions correspond to  $\varphi = \pi/2, \theta = \pi/2$  ( $\mathbf{H} \perp \mathbf{b}$ ) and  $\varphi = \pi/2, \theta = 0$  ( $\mathbf{H} \parallel \mathbf{b}$ ).

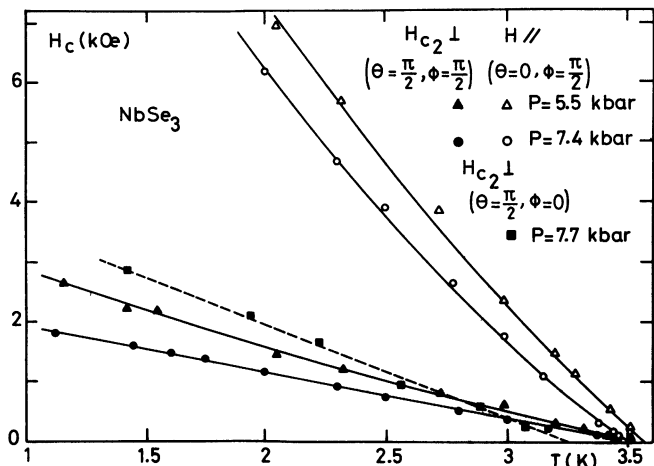


Fig. 6. — Variation of the critical magnetic fields as a function of the temperature for three different orientations. At 7.7 kbar for  $\theta = \pi/2, \varphi = 0$ . At 5.5 and 7.2 kbar for  $\varphi = \pi/2, \theta = \pi/2$  and for  $\varphi = \pi/2, \theta = 0$ .

CDW. The extrapolation towards zero of the critical field  $H_{\perp}$  ( $\theta = \pi/2, \varphi = \pi/2$ ) and  $H_{\parallel}$  ( $\theta = 0, \varphi = \pi/2$ ) gives the same critical temperatures as those obtained in zero field. We observe a slight upward curvature in the temperature variation of  $H_{\parallel}$  for the two pressures and for  $H_{\perp}$  ( $\theta = \pi/2, \varphi = \pi/2$ ) at 5.5 kbar. Such behaviour has already been reported in two-dimensional dichalcogenides and is characteristic of anisotropic superconductors [20]. In table I we give the slopes  $dH_{\perp, \parallel}/dT$  near  $T_c$  for the three pressures. Critical magnetic fields have also been measured in tantalum doped samples but without studying the anisotropy in the transverse orientation [8]. Thus we can only compare the  $dH_{\parallel}/dT$ .

The critical fields in a multilayered superconducting material can be calculated using the model of Lawrence and Doniach of Josephson coupled planes [21]. When  $H$  is perpendicular to the planes, the fluxoids have a circular cross section and the vortex current circulates freely as for a bulk superconductor. In this case the critical field  $H_{c_{2\perp}} = \varphi_0 / 2 \pi \xi_{\parallel}^2$  where  $\varphi_0 = hc/2e$  is the flux quantum,  $\xi$  the coherence length. When  $H$  is parallel to the layers the vortex current circulates inside a layer and tunnels from one layer to another as a Josephson current. Near  $T_c$  the coherence length is much larger than the layer separation and an effective mass model can be used. The

fluxoids are ellipsoidal and the critical field is defined by :

$$H_{c_{2\parallel}} = \frac{\varphi_0}{2 \pi \xi_{\perp}^2 \xi_{\parallel}}$$

with

$$\frac{H_{c_{2\parallel}}}{H_{c_{2\perp}}} = \frac{\xi_{\parallel}}{\xi_{\perp}} = \left( \frac{m_{\perp}}{m_{\parallel}} \right)^{1/2} \quad (1)$$

Following the same model the angular dependence of  $H_{c_2}$  between the parallel and perpendicular orientations is [22] :

$$H_{c_2}(\theta) = \frac{H_{c_{2\perp}}}{(\sin^2 \theta + \varepsilon^2 \cos^2 \theta)^{1/2}} \quad (2)$$

At lower temperature the coherence length may become lower than the layers separation and the normal vortex cores are located between the layers.  $H_{c_{2\parallel}}$  largely exceeds the bulk value. For  $T < T^*$  the layers decouple and the critical field diverges. This cross over temperature between a 3D-2D behaviour has been calculated by Klemm *et al.* [23] and Boccara *et al.* [24]. The decoupling between the layers explains the upward curvature of  $H_{c_2}$  measured experimentally.

This theory of Josephson junctions has been extended to filamentary superconductors by Turkevich and Klemm [25]. They consider an assembly of filaments oriented in the  $Z$  direction which forms a lattice with dimensions  $a$  and  $b$ . When  $H$  is applied perpendicular to the chains, the vortex current follows the chain and tunnels by the Josephson effect from one chain to another as when  $H$  is parallel to the planes in a layered superconductor. When  $H$  is parallel to the chains the vortex currents are entirely Josephson tunnel currents and the system behaves as a Josephson grid. Near  $T_c$  the coherence lengths are much larger than the chains separation  $a$  and  $b$  and a generalized effective mass model can be described. In the perpendicular orientation the conductivity is no longer isotropic and the angular azimuthal dependence of  $H_{c_2}$  becomes :

$$H_{c_{2\perp}}(\varphi) = \frac{\varphi_0}{2 \pi \xi^2} \frac{1}{(\varepsilon_x^2 \cos^2 \varphi + \varepsilon_y^2 \sin^2 \varphi)^{1/2}} \quad (3)$$

with  $\varepsilon_x = \left( \frac{m}{m_x} \right)^{1/2}$  and  $\varepsilon_y = \left( \frac{m}{m_y} \right)^{1/2}$

Table I. — Initial slopes of the critical magnetic fields  $dH/dT$  in kG/K.

	$\frac{dH_{\perp}}{dT} \left( \theta = \frac{\pi}{2}, \varphi = 0 \right)$	$\frac{dH_{\perp}}{dT} \left( \theta = \frac{\pi}{2}, \varphi = \frac{\pi}{2} \right)$	$\frac{dH_{\parallel}}{dT} \left( \varphi = \frac{\pi}{2}, \theta = 0 \right)$
NbSe <sub>3</sub>	5.5 kbar	0.90	4.62
	7.3 kbar	0.82	4.2
	7.7 kbar	1.58	
NbSe <sub>3</sub> + 5% Ta	1 bar		2.14

[8]

$m_x$  and  $m_y$ , being the effective masses respectively in the  $x$  and  $y$  directions.

The polar dependence of  $H_{c_2}$  when  $H$  is rotated from being perpendicular to parallel to the chains is :

$$H_{c_2}(\theta) = \frac{\varphi_0}{2\pi\xi^2} \frac{1}{\varepsilon_y} \frac{1}{(\sin^2\theta + \varepsilon_x^2 \cos^2\theta)^{1/2}} \quad (4)$$

At low temperatures the vortex core can fit between the chains. Below  $T < T^*$  the chains decouple leading to the divergence of the critical magnetic field but  $T^*$  is not the same when  $H$  is parallel or perpendicular to the chains.

Such a model can be applied to NbSe<sub>3</sub>. The structure can be seen as infinite planes of chains two atoms thick separated by Van der Waals gaps parallel to the  $(b, c)$  plane. In the transverse orientation ( $\theta = \pi/2$ ) at 7.4 kbar the extrapolation at  $T = 0$  of  $H_{c_1}$  gives a coherence length  $\xi(0) = 360 \text{ \AA}$  much larger than the chain separation. Consequently the effective mass model near  $T_c$  is applicable to NbSe<sub>3</sub>. We find that  $H_{c_1}$  is greater for  $\varphi = 0$  than for  $\varphi = \pi/2$  indicating a lower effective mass in this direction. The ratio between  $H_{c_1}(\varphi = 0, \theta = \pi/2)$  and  $H_{c_1}(\varphi = \pi/2, \theta = \pi/2)$  is equal to 2 which corresponds to an effective mass ratio of 4. Anisotropy in the transverse orientation has been measured by magnetoresistance and Shubnikov-de Haas oscillation studies. A ratio of 3 between the cyclotron effective masses in the same orientations ( $\varphi = 0, \theta = \pi/2$ ) and ( $\varphi = \pi/2, \theta = \pi/2$ ) has been measured [26] which is in a relatively good agreement with the value obtained from the anisotropy of the superconducting critical fields.

We show in figure 7 the polar dependence of the critical field as a function of  $\theta$ . We have drawn in the same figure the theoretical variation given by equation (4) with the transverse critical field equals to 1.15 kOe. The best fit is obtained with  $\varepsilon_x = 0.1820$  which is in excellent agreement with the value of

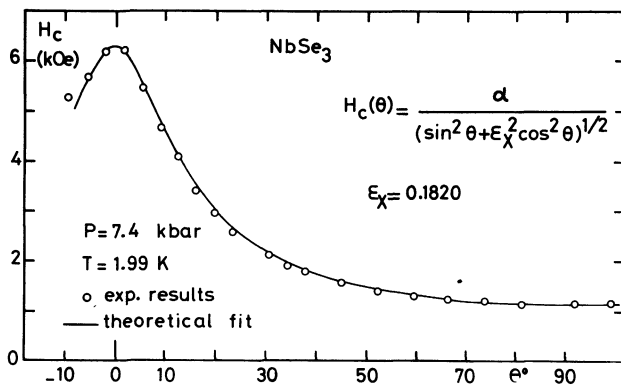


Fig. 7. — Angular dependence of the critical magnetic field at 7.2 kbar as a function of the polar angle  $\theta$ . The curve is the theoretical variation (Eq. (4)).

0.1849 obtained by the ratio of the critical fields with  $\varphi = \pi/2, \theta = \pi/2$  and  $\varphi = 0, \theta = \pi/2$ . This model gives an anisotropy of 30 between the effective masses when the electrons are travelling parallel to  $\mathbf{b}$  or parallel to  $\mathbf{c}$ . This result is in good agreement with the anisotropy of conductivity measured by Ong and Brill [27].

The upward curvature of  $H_{c_1}$  indicates the strong anisotropy of NbSe<sub>3</sub> and some decoupling between chains at low temperature in agreement with a Josephson coupled chains description. It must be noted that the analysis of the critical fields under pressure shows that NbSe<sub>3</sub> is three-dimensional near  $T_c$  with some decoupling between chains at lower temperatures. This is the opposite of the statement of Buhrman *et al.* [12] where they expect that individual planes to become superconducting around 2 K and these planes to couple together at lower temperatures to form a 3D superconductor.

**4. Conclusions.** — We have studied the low temperature properties of NbSe<sub>3</sub>. The behaviour under pressure is completely different from that at ambient pressure when we apply sufficient pressure to destroy the lower CDW transition ( $T_2 = 59 \text{ K}$  at  $P = 0$ ). NbSe<sub>3</sub> is a bulk superconductor with a total Meissner effect. The total diamagnetism has been observed with initial susceptibility measurements and the magnetization curves are typical of an irreversible type II superconductor with strong flux trapping. Due to the morphology of NbSe<sub>3</sub> with a large anisotropy in the orientation perpendicular to the chains, the effective mass model of Josephson coupled chains is reasonable near  $T_c$ . From the anisotropy of the critical fields we find a ratio of effective masses in the plane perpendicular to  $b$  of 4 and 30 in the plane  $(a^*, b)$  which is in good agreement with values obtained from Shubnikov-de Haas oscillations and conductivity anisotropies.

At ambient pressure, pure NbSe<sub>3</sub> shows a drop in resistivity at 2.2 K and a very small diamagnetism is measured at very low temperature. Powdered samples show a zero resistance below 0.9 K. Doped samples show also zero resistance but no total Meissner effect has yet been reported. We consider that, unlike NbSe<sub>3</sub> under pressure, this superconductivity is not a bulk effect but due to barriers between domains in the sample.

**Acknowledgments.** — We would like to thank A. Meerschaut, P. Molinié, and J. Rouxel from the Laboratoire de Chimie Minérale de Nantes for providing us with the samples and M. Papoular and M. Renard for helpful discussions.

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