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Superconductivity of niobium phosphorous sulphide, NbPS, prepared at high pressure

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Abstract. Electrical resistivity and dc susceptibility of NbPS prepared at high pressure have been studied at low temperatures. The compound showed a superconducting transition at around 12 K. The resistance of NbPS was measured as a function of an applied magnetic field at constant temperature. The upper critical field obtained from this data was 17 tesla (T) at 0 K. This is the highest value reported in phosphide superconductors. The coherence length of the compound was found to be 44.0 Å. Adiabatic specific-heat measurements on NbPS were performed in the temperature range 2 and 20 K. The heat capacity fitted to the expression $C = \gamma T + \beta T^3$, by a least squares analysis, yielded the values $\gamma = 6.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 0.6 \text{ mJ mol}^{-1} \text{ K}^{-4}$. The Debye temperature (Θ_D) of NbPS was found to be 330 K. The density of states at the Fermi level was calculated to be 0.51 states $\text{eV}^{-1}/\text{atom}$.

1. Introduction

Interesting ternary metal compounds NbPS, NbPSe and TaPS are prepared by reaction of the elements in 1:1:1 atomic ratio with a high pressure apparatus at around 1200 °C and 6.5 GPa. The compound NbPS is metallic, transforming to a superconductor at around 12 K [1]. In contrast, NbPSe and TaPS do not show superconductivity down to 2 K. The crystal structure of NbPS is orthorhombic with space group *Immm*, and is shown in figure 1. There are several interesting features in the structure. The Nb atoms are eightfold coordinated by four P and four S atoms at the corners of a bicapped trigonal prism [1]. The prisms share faces, resulting in the formation of Nb–Nb dimers. The inter-atomic distance of 2.93 Å in the Nb–Nb dimers is in agreement with the sum obtained from the atomic radii. The S atoms are coordinated by four Nb atoms at the corners of a distorted tetrahedron, while the P atoms form continuous strings in the *c*-axis direction with alternating short (2.22 Å) and long (2.51 Å) distances. The short distances are within the normal P–P covalent bonds found in many phosphides. Keszler and Hoffmann have carried out the tight-binding band calculations for NbPS, and discussed the origin of the high superconducting transition temperature (T_c) in the compound [2].

Several phosphide superconductors with T_c above 10 K have been found; ZrRuP and HfRuP with the Fe_2P -type structure have T_c of about 13 K [3–5], and ZrRu_4P_2 shows a superconducting transition around 11 K [6]. The upper critical fields (H_{c2}) of these phosphides are 16 tesla (T) for ZrRuP [7], 14 T for HfRuP [7] and 12.2 T for ZrRu_4P_2 [6].

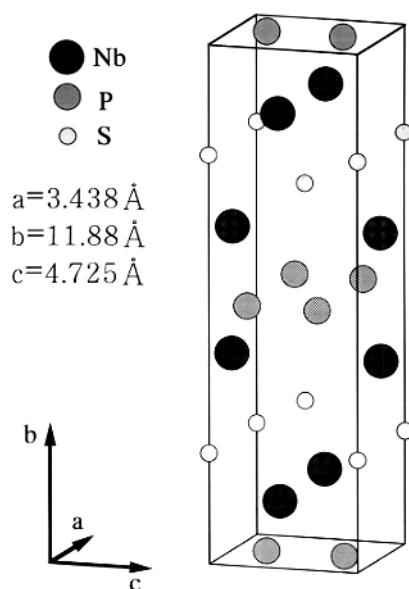


Figure 1. Crystal structure of NbPS: the lattice constants obtained by Donohue and Bierstedt [1] are shown in this figure.

We have prepared NbPS at high temperatures and high pressures, and studied the specific heat and the upper critical field of the compound at low temperatures. In this paper the superconducting properties of NbPS are discussed.

2. Experiment

Using a wedge-type cubic-anvil high pressure apparatus [4], the compound NbPS was prepared at high temperatures and high pressures. The upper and lower stages of the high pressure apparatus consisted of three anvils that slid on the wedge formed in shallow V-shaped grooves. The anvil movement was completely synchronized by means of a wedge system. The anvils consisted of cemented tungsten carbide having a $16 \times 16 \text{ mm}^2$ top-square face. The pyrophyllite sample container was formed into a 21 mm edged cube. The sample assembly for the preparation of NbPS is similar to that used for the synthesis of black phosphorus [8]. The starting materials were put into a crucible made of BN. The crucible, with a graphite heater, was then inserted into the pyrophyllite cube.

NbPS was prepared by the reaction of stoichiometric Nb, P and S or NbP and S powders at around 5 GPa, and at temperatures between 1100 and 1300 °C. NbPS prepared at high pressure was annealed at around 1000 °C for a week in the argon atmosphere. The compound prepared at high pressure was identified by powder x-ray diffraction using Cu $K\alpha$ radiation and silicon as a standard. The diffraction lines of the compound were assigned by indexing the orthorhombic structure. The lattice constants obtained from these data were $a = 3.443(2) \text{ \AA}$, $b = 11.919(4) \text{ \AA}$, $c = 4.733(1) \text{ \AA}$ and $V = 194.2 \text{ \AA}^3$. These data are in good agreement with results obtained by Donohue and Bierstedt [1]. The NbPS stoichiometry was confirmed by EPMA.

Copper or gold leads were attached to polycrystals of the samples using silver filled by epoxy contacts, and four-lead electrical resistivity measurements were then performed at low temperatures. The dc magnetic susceptibility of the polycrystalline samples was measured in

the range of 1.8–300 K using a Quantum Design SQUID magnetometer. The resistance of NbPS was measured as a function of the applied magnetic field at constant temperature [5]. The adiabatic specific-heat measurement for NbPS was performed in the temperature range between 2 and 20 K [9].

3. Results and discussion

Figure 2 shows the resistivity–temperature curve for NbPS prepared at around 1300 °C and 5 GPa. The compound was annealed at around 1000 °C for a week. The resistivity decreases with decreasing temperature, and sharply drops at around 12 K. The T_c values observed for NbPS were between 9 and 13 K. Superconductivity in NbPS was found to be sensitive to both the preparation and annealing temperatures. Figure 3 shows the temperature dependence of the dc magnetic susceptibility measured in an applied field of 5 Oe for the polycrystalline sample of NbPS. ZFC and FC show data for warming after cooling in zero field, and for cooling in the field. The existence of hysteresis between zero-field cooling (ZFC) and field cooling (FC) indicates that the compound is a type II superconductor. The susceptibility of NbPS is essentially temperature independent in the region 10–300 K. This is indicative of Pauli paramagnetism and is consistent with metallic behaviour, which is expected from the temperature dependence of the resistivity.

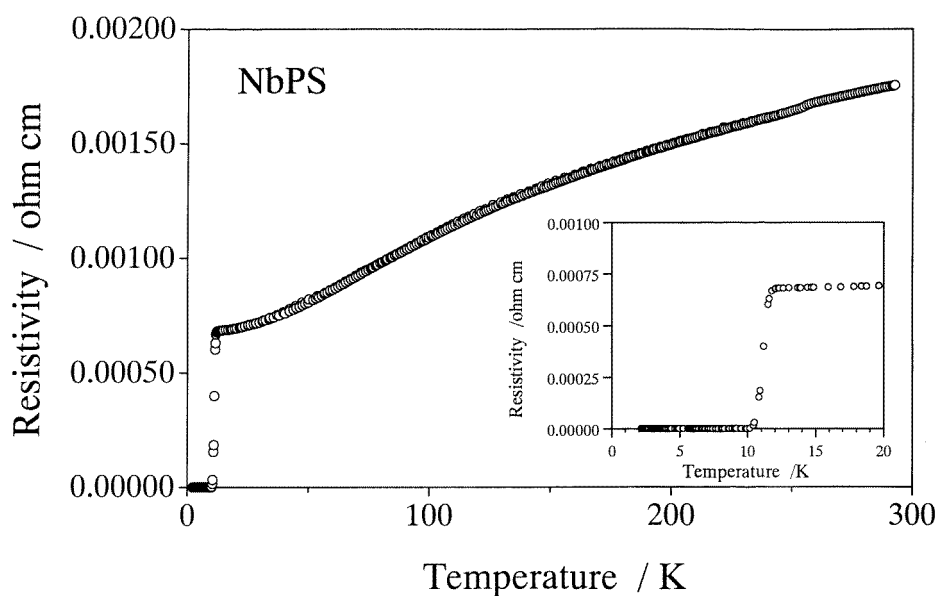


Figure 2. Electrical resistivity–temperature curve of NbPS at low temperatures.

Figure 4 shows the resistance of NbPS plotted as a function of the applied magnetic field at constant temperatures between 4 and 12 K. The superconducting transition of the compound becomes broader at low temperatures. Figure 5 shows the upper critical field (H_{c2})–temperature curve for NbPS. The temperature in which the resistance becomes zero (below $10^{-6} \Omega$) is taken as the T_c value. The H_{c2} –temperature curve was fitted to the pair breaking model [10] and is shown by the dotted line. The H_{c2} obtained from this data is 17 T at 0 K. This value is highest

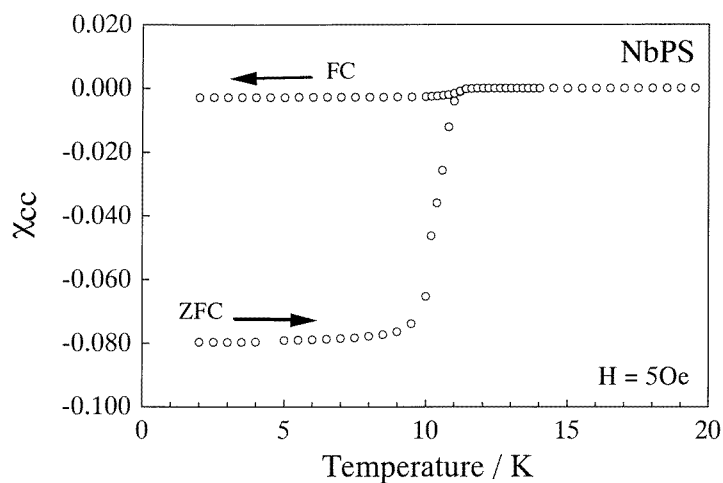


Figure 3. Temperature dependence of the dc magnetic susceptibility measured in an applied field of 5 Oe for the polycrystalline sample of NbPS.

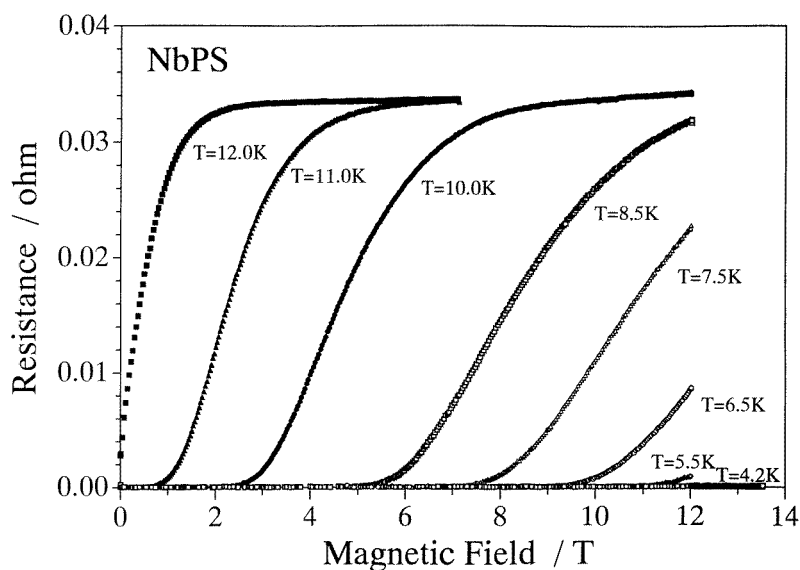


Figure 4. Resistances of NbPS plotted as a function of the applied magnetic field at constant temperatures between 4 and 12 K.

observed in the phosphide superconductors [6, 7]. The coherence length (ξ) of the compound can be estimated from the formula

$$H_{c2} = \Phi_0 / 2\pi\xi^2 \quad (1)$$

which yields a value for the coherence length of NbPS of 44.0 Å.

Figure 6 shows the result of the specific heat measurements on NbPS at low temperatures. The heat capacity (C) of the compound can be fitted to the expression $C = \gamma T + \beta T^3$ using a least squares analysis, which yields the values $\gamma = 6.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and

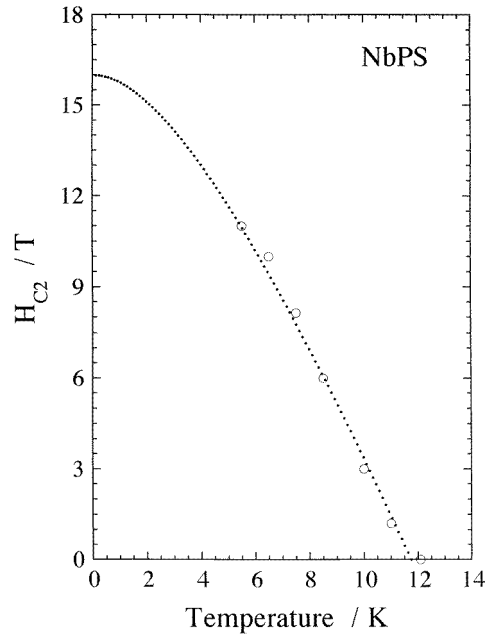


Figure 5. H_{c2} -temperature curve of NbPS; the dotted curve is fitted to the pair breaking model [10]; the open circles are the T_c values measured by us.

$\beta = 0.16 \text{ mJ mol}^{-1} \text{ K}^{-4}$. In the normal state, $T > T_c$, the coefficient γ is related to the electronic density of states at the Fermi energy, $N(0)$

$$\gamma = \frac{\pi^2}{3} n N_0 k_B^2 N(0) (1 + \lambda) \quad (2)$$

where n is the number of atoms per formula unit, N_0 is Avogadro's number, k_B is the Boltzmann constant and λ is the electron-phonon coupling parameter given by McMillan. The coefficient β is related to the Debye temperature (Θ_D) as

$$\beta = \frac{12}{5} \pi^4 n N_0 k_B / \Theta_D^3. \quad (3)$$

Using the above data the Debye temperature of NbPS was calculated as 330 K.

In order to derive $N(0)$, the McMillan formula for λ may be used [11],

$$\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu^*) \ln(\Theta_D/1.45T_c) - 1.04} \quad (4)$$

where μ^* was taken to be 0.1 [12, 13]. The parameters for NbPS were found to be 0.81 for λ and 0.51 states $\text{eV}^{-1}/\text{atom}$ for $N(0)$. The density of states at the Fermi level found for NbPS is low, though the T_c is relatively high. Stewart *et al* have carried out low temperature specific measurements on the ternary equiatomic phosphides ZrRuP and HfRuP, which have T_c values of about 13 K [13]. For these materials, the electronic density of states at the Fermi level was found to be 0.76 states $\text{eV}^{-1}/\text{atom}$ for ZrRuP and 0.74 states $\text{eV}^{-1}/\text{atom}$ for HfRuP, indicating that the density of states at Fermi level for MRuP ($M = \text{Zr}$ and Hf) is relatively higher than that found in NbPS.

The superconducting data of the ternary equiatomic compounds NbPS and ZrRuP are summarized in table 1. The number of valence electrons/formula unit is 16 for NbPS and

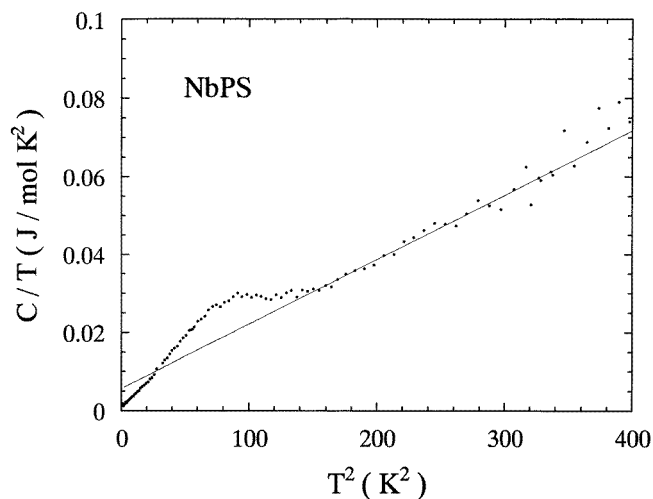


Figure 6. Specific heat of NbPS at low temperatures; the line fitted using a least squares analysis is shown.

Table 1. Superconducting data of ternary equiatomic compounds NbPS and ZrRuP.

	NbPS	ZrRuP
Valance electrons/formula unit	16	17
Structure	Orthorhombic	Hexagonal
Cell volume/formula unit [cm ³]	48.25	45.50
T_c [K]	13	13
H_{c2} [T]	17	16 [7]
ξ [Å]	44.0	45.4 [7]
Θ_D [K]	330	345 [13]
λ	0.81	0.79 [13]
$N(0)$ [states eV ⁻¹ /atom]	0.51	0.76 [13]

17 for ZrRuP. ZrRuP is a metal-rich compound and NbPS is a non-metal-rich compound. However, the T_c and H_{c2} values of NbPS are close to those of ZrRuP. These results suggest that the band structures of both compounds near the Fermi level are mostly d orbital in character.

As the P atoms in NbPS form continuous strings in the c -axis with alternating short and long distances, and the short distances are in agreement with that expected of normal P–P covalent bonds, and if it is assumed that only the P atoms separated by the short distance are bonded, then the valences in NbPS can be regarded as being 2Nb^{4+} , $(\text{P}_2)^{4-}$ and 2S^{2-} . Since Nb–Nb dimers with a d^1 electron configuration would be formed in the NbPS structure, the semiconductive behaviour would be anticipated, as is found in NbI_4 , where the Nb–Nb dimers in the linear chain structure behave as a semiconductor [14, 15]. However, in the case of NbPS, as the long P–P distances contain some bonding character, the valence of Nb must be lower, being somewhere between Nb^{4+} and Nb^{3+} [1]. Thus, NbPS can become metallic. Keszler and Hoffmann have performed tight binding band structure calculations for NbPS [2]. The bands of NbPS near the Fermi level are mostly of Nb d-orbital character and below they have P and S character. The d_{yz} band is flat in a large portion of the Brillouin zone, affording a peak in the

density of states at the Fermi level. The presence of this band may be correlated to the high superconducting transition temperature.

References

- [1] Donohue P C and Bierstedt P E 1969 *Inorg. Chem.* **8** 2690
- [2] Kesler D A and Hoffmann R 1987 *J. Am. Chem. Soc.* **109** 118
- [3] Barz H, Ku H C, Meisner G P, Fisk Z and Matthias B T 1980 *Proc. Natl Acad. Sci. USA* **77** 3132
- [4] Shirovani I, Ichihashi N, Nozawa K, Kinoshita M, Yagi T, Suzuki K and Enoki T 1993 *Japan. J. Appl. Phys. Suppl.* **32** 695
- [5] Shirovani I, Tachi K, Takeda K, Todo S, Yagi T and Kanoda K 1995 *Phys. Rev. B* **52** 6197
- [6] Shirovani I, Iwasaki G, Kaneko I, Sekine C, Todo S and Yagi T 1997 *Solid State Commun.* **104** 217
- [7] Shirovani I, Tachi K, Konno Y, Todo S and Yagi T 1999 *Phil. Mag. B* **79** 767
- [8] Shirovani I 1982 *Mol. Cryst. Liq. Cryst.* **86** 1943
- [9] Shirovani I, Uchiyama T, Ohno K, Sekine C, Nakazawa Y, Kanoda K, Todo S and Yagi T 1997 *Phys. Rev. B* **56** 7866
- [10] Tinkham M 1975 *Introduction to Superconductivity* (New York: McGraw-Hill)
- [11] McMillan W L 1968 *Phys. Rev.* **167** 331
- [12] Meisner G P, Stewart G R, Torikachvili M S and Maple M B 1984 *LT-17* ed U Eckern, A Schmid, W Weber and H Wuhl (Amsterdam: Elsevier) p 711
- [13] Stewart G R, Meisner G P and Ku H C 1982 *Superconductivity in d- and f-Band Metals* ed W Buckel and W Weber (Karlsruhe: Kernforschungszentrum Karlsruhe) p 331
- [14] Kepert D L and Marshall R E 1974 *J. Less-Common Met.* **34** 153
- [15] Kawamura H, Matui N, Nakahata I, Kobayashi M, Akahama Y and Shirovani I 1998 *Solid State Commun.* **108** 919