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Superconductivity in ternary chalcogenides $Bi_2Ni_3X_2$ (X = S, Se)

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Abstract

The physical properties of parkerite and its related compound, $Bi_2Ni_3X_2$ (X = S, Se), were studied. The electrical resistivity of both compounds shows typical metallic behaviour up to 400 K. The resistivity and specific heat measurements at low temperatures reveal that these compounds are superconducting with a transition temperature of ∼0.7 K. The upper critical fields at 0 K, $\mu_0 H_{c2}(0)$, are 95 mT ($Bi_2Ni_3S_2$) and 75 mT ($Bi_2Ni_3Se_2$). In the normal state, the electronic specific heat coefficient, γ, and the Debye temperature, Θ_D, are found to be 11.4 mJ mol^{-1} K^{-2} and 189 K, respectively, for $Bi_2Ni_3S_2$, and 12.2 mJ mol^{-1} K^{-2} and 173 K, respectively, for $Bi_2Ni_3Se_2$. From the electronic specific heat in the superconducting temperature range, it was found these compounds belong to the weak-coupling BCS superconductors.

1. Introduction

Transition metal chalcogenides have focused interest in chemistry and materials science because of their exceptional physical and chemical properties such as charge-density-wave behaviour [1, 2], superconductivity [3, 4] and intercalation reactions [5, 6]. In addition, striking structures are observed in the mixed metal-rich chalcogenides, which form a wide variety of heterometallic bonds ranging from 1D chains in $Sc_{14}M_3Te_8$ (M = Ru, Os) [7], to 2D slabs in Ni_6SnS_2, $Ni_9Sn_2S_2$ [8] and 3D frameworks $Ta_9M_2S_6$ (M = Fe, Co, Ni) [9].

We have paid attention to the mixed metal-rich chalcogenides $A_2M_3X_2$ (A = In, Sn, Tl, Pb, Bi; M = Co, Ni, Rh, Pd; X = S, Se). Their crystal structures are grouped into two types (the shandite-type and parkerite-type structures); the compounds containing bismuth as the A ion crystallize in the parkerite-type structure [10–12]. Recently, the detailed crystal structure for parkerite $Bi_2Ni_3S_2$ was reported from its single-crystal x-ray diffraction analysis [13]. Figure 1 illustrates the crystal structure for $Bi_2Ni_3S_2$. This structure can be represented as a 3D framework formed by the heterometallic Ni–Bi (2.70–2.96 Å) and Ni–S (2.18–2.19 Å) bonds. At the same time, Ni–Ni bonds also exist. However, their distances (>2.75 Å) are substantially larger than that of metallic Ni (2.49 Å); therefore their contributions are weak. As

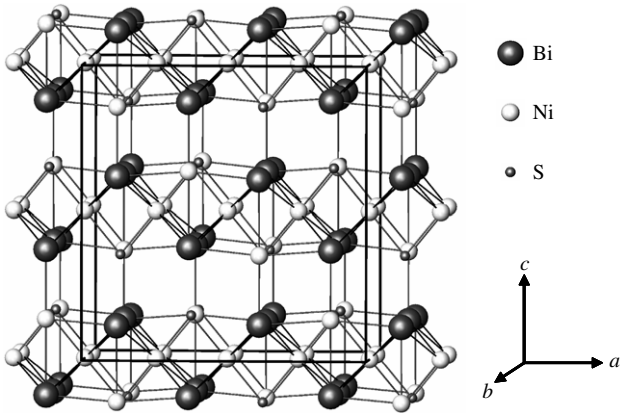

Figure 1. The crystal structure of $Bi_2Ni_3S_2$.

regards the physical properties of parkerite-related compounds, only the results of resistivity and thermopower measurements above liquid-nitrogen temperature have been reported [12].

In this paper, we have performed detailed resistivity and specific heat measurements for $Bi_2Ni_3X_2$ (X = S, Se) down to 0.4 K and found superconductivity at about 0.7 K. Their results will be reported here.

2. Experimental details

The samples were prepared from stoichiometric mixtures of the elements: Bi powder (99.9%), Ni powder (99.9%), S powder (99.99%) and Se powder (99.9%). The mixtures were pressed into pellets and then sealed in an evacuated quartz tube. To avoid reaction between the samples and the quartz tube, the tube was coated with carbon. The samples were heated at 1200 °C for 6 h and then cooled down rapidly to room temperature.

Powder x-ray diffraction measurements were carried out in the range $10° \leqslant 2\theta \leqslant 120°$ using Cu Kα radiation on a Rigaku RINT 2000 diffractometer equipped with a curved graphite monochromator. The crystal structures were determined by the Rietveld technique, using the program RIETAN 2000 [14].

Electrical resistivity measurements were carried out in the temperature range 0.4–400 K and in magnetic fields up to 150 mT by the standard four-probe method in a Quantum Design physical property measurement system (PPMS) equipped with a ^{3}He refrigerator. The sintered samples were cut into pieces having sizes of approximately $3 \times 2 \times 0.8$ mm^3 ($Bi_2Ni_3S_2$) and $7 \times 3 \times 1$ mm^3 ($Bi_2Ni_3Se_2$). Four contact wires were painted onto the samples using silver paste.

Specific heat measurements were performed by the thermal relaxation method in the temperature range between 0.4 and 15 K with the PPMS. The sintered samples (∼15 mg) were mounted on a thin alumina plate with Apiezon N grease for better thermal contact.

3. Results and discussion

3.1. X-ray powder diffraction

The $Bi_2Ni_3X_2$ (X = S, Se) phases were identified from the x-ray diffraction (XRD) profiles. The x-ray diffraction profiles for $Bi_2Ni_3S_2$ and $Bi_2Ni_3Se_2$ are shown in figures 2(a) and (b),

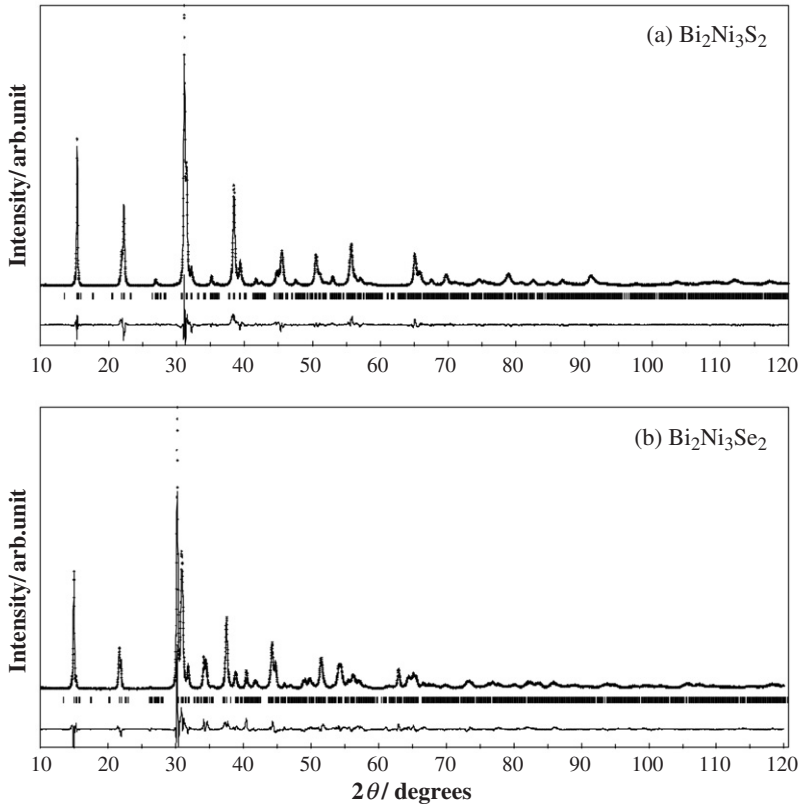

Figure 2. X-ray diffraction profiles for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$.

respectively. The profile for $Bi_2Ni_3S_2$ is indexed with a monoclinic parkerite-type cell with the space group $C2/m$. For $Bi_2Ni_3S_2$, the diffraction profile calculated by the Rietveld refinement agrees well with the observed one, and the reliability factors are 12.91% for R_{wp} and 2.98 % for R_I. The obtained lattice and positional parameters for $Bi_2Ni_3S_2$ are in good agreement with the reported parameters [13]. However, the R-factors for $Bi_2Ni_3Se_2$ are comparatively large ($R_{wp} = 16.32\%$ and $R_I = 7.12\%$). This suggests that the structure of $Bi_2Ni_3Se_2$ is not the same as that of $Bi_2Ni_3S_2$, although the modes of atomic arrangement in these structures are very similar, as mentioned previously [15].

3.2. Physical properties

Figures 3(a) and (b) show the temperature dependence of the electrical resistivity for $Bi_2Ni_3S_2$ and $Bi_2Ni_3Se_2$, respectively. These compounds show typical metallic behaviour up to 400 K. When these samples are cooled below ∼0.85 K, their resistivity drops sharply, indicating a phase transition to a superconducting state. The onset temperatures for $Bi_2Ni_3S_2$ and $Bi_2Ni_3Se_2$ are 0.85 and 0.86 K, respectively, and zero resistivities are attained below 0.75 and 0.66 K, respectively. The critical temperatures T_c are defined as the midpoint of the transition; $T_c^{\mathrm{mid},R} = 0.79$ K ($Bi_2Ni_3S_2$) and 0.73 K ($Bi_2Ni_3Se_2$).

Figure 4 shows the temperature dependence of resistivities in various magnetic fields. The values of $T_c^{\mathrm{mid},R}$ decrease with increasing applied field. Figure 5 shows the field

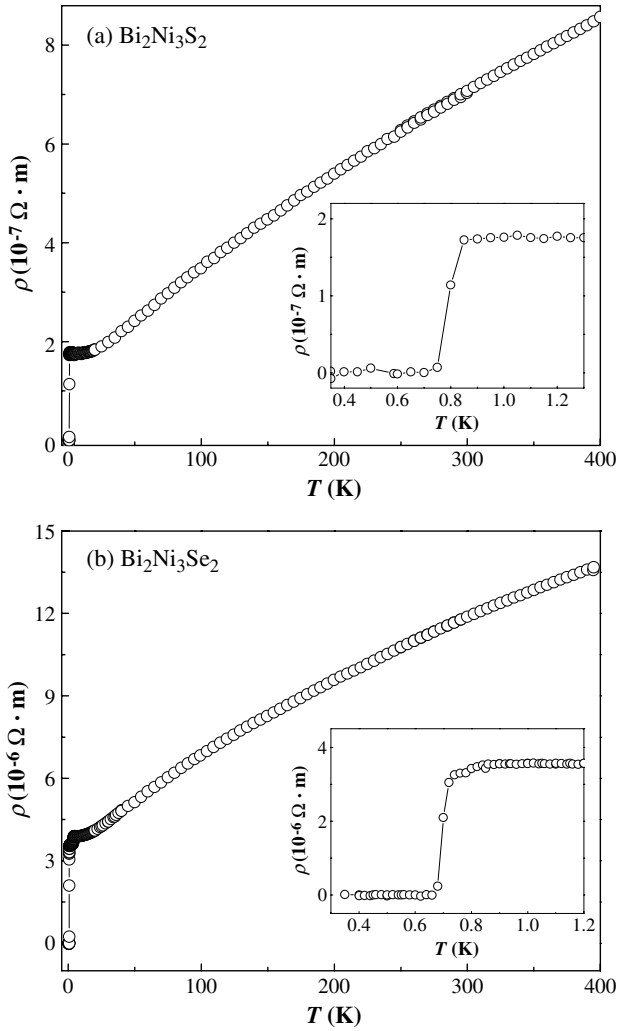

Figure 3. Temperature dependence of the electrical resistivity for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$.

dependence of resistivities at various temperatures. Assuming that both compounds are type-II superconductors, as will be justified below, the upper critical fields, $H_{c2}(T)$, were determined from figures 4 and 5. Figure 6 shows $H_{c2}(T)$ as a function of the critical temperature. According to the Werthamer–Helfand–Hohenberg (WHH) theory for a type-II superconductor in the dirty limit [16], the upper critical field at $T = 0$ K can be estimated from the relation

$$H_{c2}(0) = 0.693\, T_c \left(-\frac{\mathrm{d}H_{c2}(T)}{\mathrm{d}T}\right)_{T\sim T_c}. \tag{1}$$

The gradients $\mathrm{d}\mu_0 H_{c2}/\mathrm{d}T$ in the linear region near T_c of $Bi_2Ni_3X_2$ (X = S, Se) are found to be about -180 and -148 mT K^{-1}, respectively. Consequently, the $\mu_0 H_{c2}(0)$ values of both compounds are found to be about 95 mT ($Bi_2Ni_3S_2$) and 75 mT ($Bi_2Ni_3Se_2$). Moreover, the values of Ginzburg–Landau (GL) coherence length at zero temperature $\xi_{GL}(0)$ can be estimated

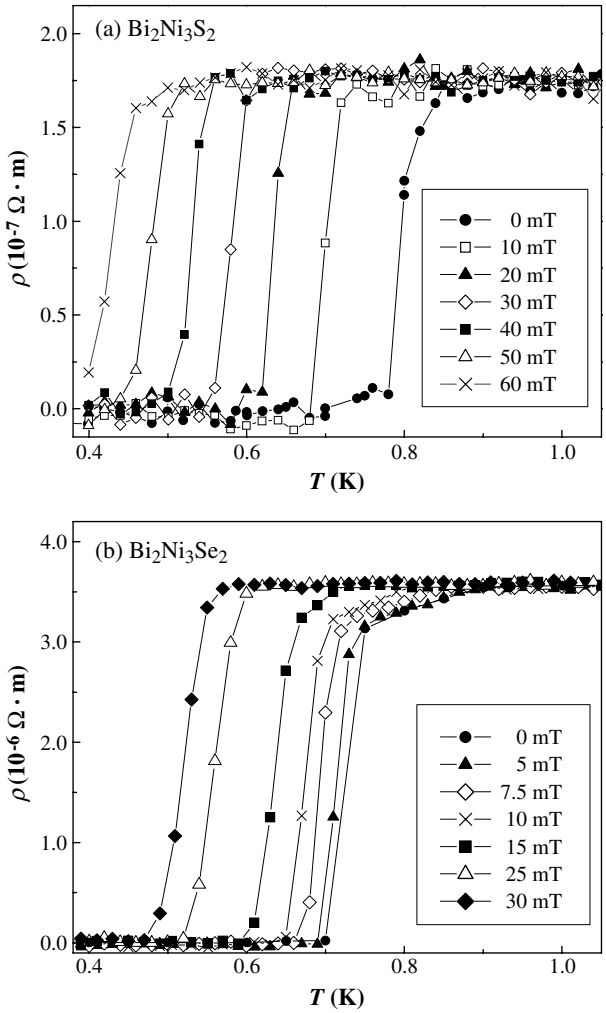

Figure 4. Temperature dependence of the electrical resistivity under various magnetic fields for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$.

to be 590 Å for $Bi_2Ni_3S_2$ and 660 Å for $Bi_2Ni_3Se_2$ by the following formula:

$$H_{c2}(0) = \frac{\Phi_0}{2\pi\mu_0\xi_{GL}(0)^2}, \tag{2}$$

where μ_0 and Φ_0 are the magnetic permeability of vacuum and quantum flux, respectively.

The temperature dependences of the specific heat for $Bi_2Ni_3S_2$ and $Bi_2Ni_3Se_2$ are shown in figures 7(a) and (b), respectively. The fact that a jump in the specific heat is observed starting at 0.79 K ($Bi_2Ni_3S_2$) and 0.73 K ($Bi_2Ni_3Se_2$) is indicative of the bulk superconducting transition. The critical temperatures from specific heat data are defined as the midpoint of the transition; $T_c^{\mathrm{mid},C} = 0.72$ K ($Bi_2Ni_3S_2$) and 0.70 K ($Bi_2Ni_3Se_2$). We assume that the total specific heat is composed of electron and lattice parts, $C(T) = C_e(T) + C_{ph}(T)$. In the normal state, the lattice part is expressed by the βT^3 term at a temperature much below the Debye temperature Θ_D, and the electronic specific heat is assumed to be the γT term, i.e.,

$$C(T)/T = \gamma + \beta T^2. \tag{3}$$

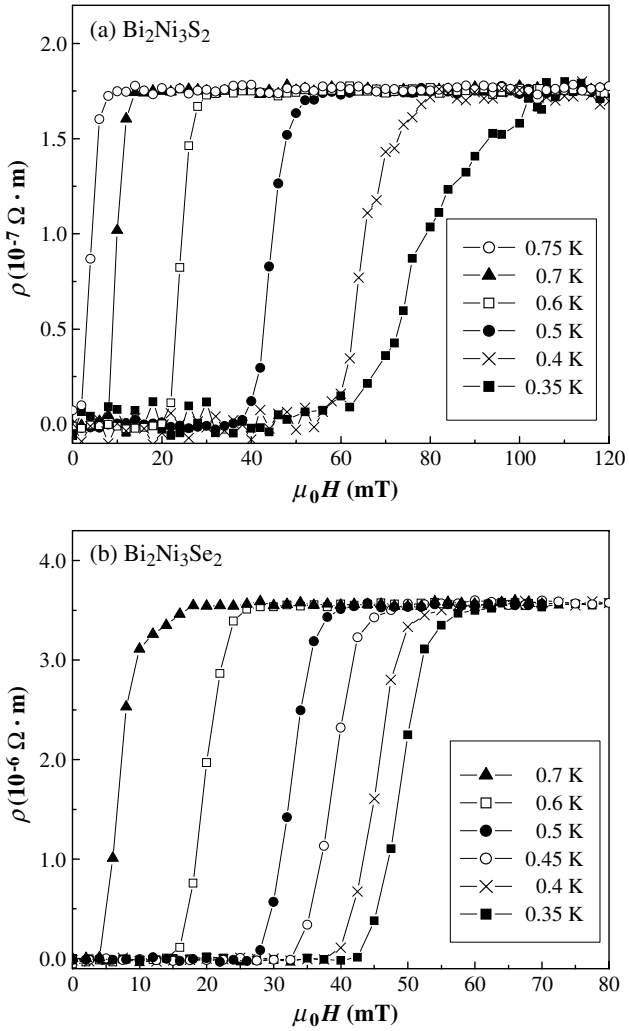

Figure 5. Magnetic field dependence of electrical resistivity at various temperatures for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$.

From the $C(T)/T$ versus T^2 plot, the γ and β values of both compounds were obtained to be 11.4(1) mJ mol^{-1} K^{-2} and 2.0(1) mJ mol^{-1} K^{-4} for $Bi_2Ni_3S_2$, and 12.2(1) mJ mol^{-1} K^{-2} and 2.6(1) mJ mol^{-1} K^{-4} for $Bi_2Ni_3Se_2$. The Debye temperature values Θ_D were then calculated to be 189 K ($Bi_2Ni_3S_2$) and 173 K ($Bi_2Ni_3Se_2$) using the formula

$$\Theta_D = \left(\frac{12n\pi^4 R}{5\beta}\right)^{1/3}, \tag{4}$$

where $R = 8.314$ J mol^{-1} K^{-1} and $n = 7$ for both compounds.

The specific heat jump ΔC at the $T_c^{\mathrm{mid},C}$ shows an evident energy gap in the superconducting state, and the change in the normalized value of $\Delta C/\gamma T_c$ at the transition temperature, as well as the evolution of heat capacity as a function of temperature below the superconducting transition, supplies important information about the nature of the

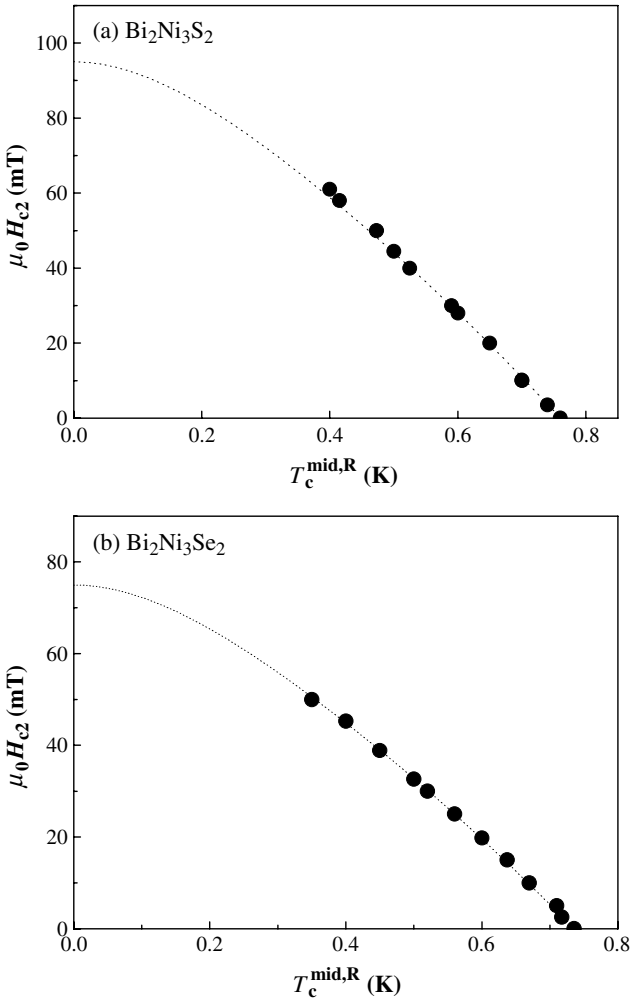

Figure 6. Temperature dependence of the upper critical fields for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$ determined from the electrical resistivity data. Dotted lines show the fitting results using the WHH theory.

superconducting mechanism. The electronic specific heat C_e was obtained by subtracting the lattice contribution estimated earlier from the total specific heat, and the temperature dependences of C_e for $Bi_2Ni_3S_2$ and $Bi_2Ni_3Se_2$ are plotted in figures 8(a) and (b), respectively. Below the superconducting transition temperature, the temperature dependences of the electronic specific heat follow an exponential decay, as seen in figure 8. On the other hand, the fitting of a T^n function gives poor results. These fitting results show that $Bi_2Ni_3S_2$ and $Bi_2Ni_3Se_2$ are s-wave superconductors. The normalized specific heat jump values $\Delta C/\gamma T_c^{mid,C}$ are 1.35 for $Bi_2Ni_3S_2$ and 1.16 for $Bi_2Ni_3Se_2$. These values are smaller than the value 1.43 expected from the BCS theory. However, these small jump values are comparable with those of weak-coupling BCS superconductors having an anisotropic-energy gap like Nb_3S_4 and Nb_3Se_4 [17, 18]. Considering the crystal structure for $Bi_2Ni_3X_2$ (X = S, Se), these compounds may also be anisotropic superconductors. Detailed confirmation of this interpretation will

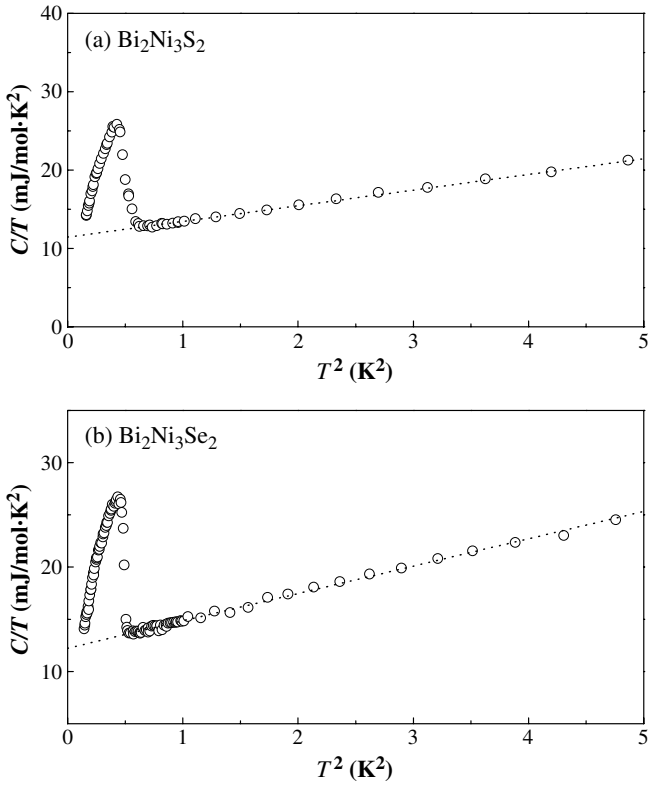

Figure 7. Temperature dependence of the specific heat for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$. The dotted lines show fitting results using equation (3).

require studies of specific heat measurements in a magnetic field, or using single crystal measurements.

The thermodynamic critical field $H_c(T)$ can be obtained as a function of temperature using the specific heat data in both the normal and superconducting state. The difference in entropy $\Delta S(T)$ between the normal and superconducting states was obtained through the thermodynamic relation

$$\Delta S(T) = S_n(T) - S_s(T) = \gamma T - \int_0^T [C_{es}(T')/T']\,dT', \tag{5}$$

where $S_n(T)$ and $S_s(T)$ are the entropies in the normal and superconducting states, and C_{es} is the electronic specific heat in the superconducting state. C_{es} below 0.4 K is extrapolated by the exponential curve. $H_c(T)$ was obtained by the relationship

$$G_n(T) - G_s(T) = \int_T^{T_c} \Delta S(T')\,dT' = \tfrac{1}{2}\mu_0 V_m H_c(T)^2, \tag{6}$$

where V_m is the molar volume. The calculated values of $\mu_0 H_c(0)$ are 6.68 mT for $Bi_2Ni_3S_2$ and 6.39 mT for $Bi_2Ni_3Se_2$.

On the other hand, the BCS theory predicts the magnitude of $H_c(0)$ by the relation

$$H_c(0) = \left[\frac{0.47\gamma T_c^2}{\mu_0 V_m}\right]^{1/2}. \tag{7}$$

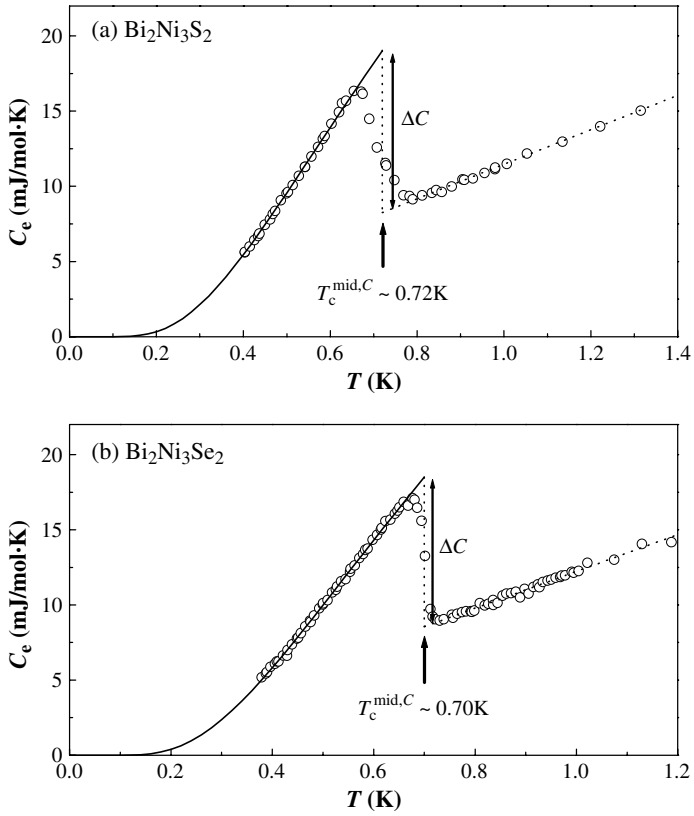

Figure 8. Temperature dependence of the electronic specific heat for (a) $Bi_2Ni_3S_2$ and (b) $Bi_2Ni_3Se_2$. The solid lines show fitting results using exponential functions.

Taking the experimental values for both compounds into equation (7) gives 6.74 mT ($Bi_2Ni_3S_2$) and 6.61 mT ($Bi_2Ni_3Se_2$), which are close to the values from equation (6). Moreover, the penetration depth $\lambda(0)$, GL parameter $\kappa(0)$ and lower critical field at 0 K $H_{c1}(0)$ are estimated from the following relations:

$$H_C(0) = \frac{\Phi_0}{2\sqrt{2}\pi\mu_0\lambda(0)\xi_{GL}(0)}, \tag{8}$$

$$\kappa(0) = \frac{\lambda_{GL}(0)}{\xi_{GL}(0)}, \tag{9}$$

$$H_{c1}(0) = \frac{H_c(0)}{\sqrt{2}\kappa}\ln\kappa. \tag{10}$$

By using the value of $H_c(0)$ obtained from equation (6), $\lambda(0)$, $\kappa(0)$ and $\mu_0 H_{c1}(0)$ are estimated to be 5919 Å, 10.1 and 1.08 mT, respectively, for $Bi_2Ni_3S_2$, and 5497 Å, 8.3 and 1.15 mT, respectively, for $Bi_2Ni_3Se_2$. These superconducting parameters are summarized in table 1. The values of $\kappa(0)$ strongly suggest that both of the compounds are typical type-II superconductors.

Table 1. Superconducting and normal-state properties for $Bi_2Ni_3X_2$ (X = S, Se).

	$Bi_2Ni_3S_2$	$Bi_2Ni_3Se_2$
V_m (m^3 mol^{-1})	7.75×10^{-5}	8.14×10^{-5}
$T_c^{mid,R}$ (K)	0.76	0.73
$T_c^{mid,C}$ (K)	0.72	0.70
$\mu_0 H_{c2}(0)$ (mT)	95	75
$\xi_{GL}(0)$ (Å)	590	660
γ (mJ mol^{-1} K^{-2})	11.4	12.2
Θ_D (K)	189	173
$\Delta C/\gamma T_c^{mid,C}$	1.35	1.16
$\mu_0 H_c(0)$ (mT)[a]	6.7	6.4
$\lambda(0)$ (Å)	5900	5500
$\kappa(0)$	10.1	8.3
$\mu_0 H_{c1}(0)$ (mT)	1.08	1.15

[a] The values of $\mu_0 H_c(0)$ are obtained from equation (6).

4. Summary

We found that the two ternary metal-rich chalcogenides $Bi_2Ni_3X_2$ (X = S, Se) are superconductors with a critical temperature, T_c, of about 0.7 K, and examined their physical properties in detail by electrical resistivity and specific heat measurements. The $\mu_0 H_{c2}(0)$ values are estimated from the midpoint temperatures of electrical resistivity under the magnetic fields to be about 95 mT ($Bi_2Ni_3S_2$) and 75 mT ($Bi_2Ni_3Se_2$). From specific heat measurements, γ, Θ_D and $\Delta C/\gamma T_c$ are 11.4 mJ mol^{-1} K^{-2}, 189 K and 1.35, respectively, for $Bi_2Ni_3S_2$, and 12.2 mJ mol^{-1} K^{-2}, 173 K and 1.16, respectively, for $Bi_2Ni_3Se_2$. Study of the specific heat in the superconducting state suggests that both compounds are categorized as weak-coupling BCS, s-wave superconductors. The small specific heat jump is indicative of anisotropic superconductivity.

References

[1] Waintal A, Meerschaut A, Molinite P and Rouxel J 1976 *Solid State Commun.* **20** 759–63
[2] Wilson J A, Di Salvo F J and Mahajan S 1974 *Phys. Rev. Lett.* **32** 882–5
[3] Hagino T, Seki Y, Wada N, Tsuji S, Shirane T, Kumagai K and Nagata S 1995 *Phys. Rev.* B **51** 12673–84
[4] Matthias B T, Marezio M, Barz H F, Corenzwit E, Cooper A S and Barz H E 1972 *Science* **175** 1465–6
[5] Dines M B 1975 *Mater. Res. Bull.* **10** 287–91
[6] Canadell E, Thieffry C, Mathey Y and Whangbo M-H 1989 *Inorg. Chem.* **28** 3043–7
[7] Chen L and Corbett J D 2003 *J. Am. Chem. Soc.* **125** 1170–1
[8] Baranov A I, Isaeva A A, Kloo L and Popovkin B A 2003 *Inorg. Chem.* **42** 6667–72
[9] Harbrecht B and Franzen H F 1985 *J. Less-Common Met.* **113** 349–60
[10] Peacock M A and McAndrew J 1950 *Am. Mineral.* **35** 425–39
[11] Zabel M, Wandinger S and Range K-J 1979 *Z. Naturf.* B **34** 238–41
[12] Natarajan S and Subba Rao G V 1988 *J. Less-Common Met.* **138** 215–24
[13] Baranov A I, Olenev A V and Popovkin B A 2001 *Russ. Chem. Bull.* **50** 353–8
[14] Izumi F and Ikeda T 2000 *Mater. Sci. Forum* **321–324** 198–203
[15] Clauss A 1977 *Naturwissenschaften* **64** 145
[16] Werthamer N R, Helfand E and Hohenberg P C 1966 *Phys. Rev.* **147** 295–302
[17] Okamoto H and Ishihara Y 1993 *Phys. Rev.* B **48** 3927–32
[18] Okamoto H, Taniguti H and Ishihara Y 1996 *Phys. Rev.* B **53** 384–8