

HEAT CAPACITY OF INTERCALATED LAYERED MATERIALS Fe_xNbS_2 AT LOW TEMPERATURE

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Abstract

The heat capacities and magnetic susceptibilities of powdered samples of Fe_xNbS_2 ($x=0.14$, 0.21 and 0.30) were measured at temperatures from 8 to 303 K and from 5 to 300 K, respectively. For $\text{Fe}_{0.14}\text{NbS}_2$, the magnetic susceptibility exhibited an anomaly as a shoulder at about 57 K, but no heat capacity anomaly was observed at this temperature, indicating the appearance of a spin-glass state. Anomalies in the heat capacity for Fe_xNbS_2 ($x=0.21$ and 0.30) occurred at 100.5 and 45.0 K, respectively, where the magnetic susceptibility displayed a maximum, corresponding to an antiferro-paramagnetic phase transition. The electronic state of the iron atom is discussed on the basis of entropy analysis.

Keywords: Fe_xNbS_2 , heat capacity, intercalated compounds, layered compounds, magnetic susceptibility

Introduction

A number of transition metal dichalcogenides form intercalated layered compounds, where weak van der Waals bonding between chalcogen atoms of adjacent layers allows easy intercalation of the metallic atoms. These metal intercalated materials are of potential use as cathodes in high-energy-density secondary batteries. Among intercalated layered compounds, the iron atoms in Fe_xNbS_2 can occupy the vacant octahedral sites situated between the prismatic layers [S-Nb-S], and form ordered structures for the compositions with $x=1/4$ and $1/3$. The crystal structures of both compounds are related to the NbS_2 -2s type (a and c in a hexagonal cell), with the Fe ions forming an ordered superlattice ($2a$ and c in $\text{Fe}_{1/4}\text{NbS}_2$; $a\sqrt{3}$ and c in $\text{Fe}_{1/3}\text{NbS}_2$) [1, 2].

The phase relations of iron niobium sulfides, $(\text{Fe}_y\text{Nb}_{1-y})_{1+x}\text{S}_2$, at high temperatures were studied as a function of sulfur partial pressure by Wakihara *et al.* [3] and

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Hinode *et al.* [4]. They reported that niobium dissolved in the Fe–S system with difficulty, but that iron dissolved in the Nb–S system in amounts up to 35 mol% ($y=0.35$).

Friend *et al.* [5] measured the resistivity, Hall effect and magnetic susceptibility as functions of temperature for the first row transition metal intercalates of niobium disulfide, $M_{1/3}\text{NbS}_2$ ($M=\text{Mn, Fe, Co and Ni}$). Metallic behaviour, associated with electrical conduction in the niobium d bands, was observed, and sharp anomalies of the magnetic susceptibility were seen at the temperatures at which the magnetic moments localized on the intercalated ions order. The magnetic behaviour is related to the intercalated ions, which possess localized moments. The Mn intercalation complex exhibits a ferromagnetic order, whereas the Fe, Co and Ni complexes have an antiferro-magnetic order.

Gorochov *et al.* [6] also measured the resistivity, Hall voltage and magnetic susceptibility and Mössbauer parameters of $\text{Fe}_{1/4}\text{NbS}_2$ and $\text{Fe}_{1/3}\text{NbS}_2$ as powders and as single-crystals in the temperature range from 4.2 to 300 K. Magnetic susceptibility and Mössbauer experiments revealed that these compounds have antiferro-magnetic order below 137 and 47 K, respectively; the magnetic moments in the antiferro-magnetic state are parallel to the c -axis. Two anomalies are observed in the electrical properties of $\text{Fe}_{1/4}\text{NbS}_2$, evidenced by a steep increase in the resistivity when the temperature decreases, and by an abrupt change in the sign of the Hall coefficient at around 110 and 40 K, respectively. Metallic behaviour is observed in both compounds. A comparative Mössbauer study demonstrated that the ionic Fe^{2+} behaviour involving a high-spin state is more pronounced in $\text{Fe}_{1/4}\text{NbS}_2$ than in $\text{Fe}_{1/3}\text{NbS}_2$.

Magnetic measurements of randomly intercalated polycrystalline Fe_xNbS_2 ($0.11 \leq x \leq 0.5$) were made by Doi and Tazuke [7]. They reported that the oxidation state of the Fe atoms is likely to be only Fe^{2+} , since the effective magnetic moment determined by assuming the Curie-Weiss law at high temperatures is close to $4.9 \mu_B$ for $S=2$ and $g=2$. They also reported that a spin-glass state exists for the compositions $x \leq 0.3$, as indicated by the different behaviour between field-cooled (FC) and zero-field-cooled (ZFC) magnetizations at low temperatures.

The electrical and magnetic properties of Fe_xNbS_2 have been studied mainly for these two compositions $x=1/3$ and $x=1/4$, where the magnetic transition temperature depends markedly on the composition. However, the heat capacity has not been measured for any compositions so far. In the present study, the heat capacity and magnetic susceptibility of powdered samples of Fe_xNbS_2 ($x=0.14, 0.21$ and 0.30) have been measured below 300 K as functions of temperature.

Experimental

The starting materials used for sample preparation were high-purity iron (99.998%), niobium (99.9%) and sulfur (99.99%). A mixture of iron, niobium and sulfur having the given concentrations was placed into a silica capsule, which was then evacuated and finally sealed under vacuum. The mixture was reacted for 24 h at 400°C and for 24 h at 900°C in an evacuated silica tube. The sample was then ho-

mogenized for one week at 900°C and heat-treated for one week at 300°C. The iron contents in each sample were determined by using the relation between the lattice constants of the *c*-axis and the iron contents determined by electron probe micro analysis and X-ray diffractometry of single-crystals of Fe_xNbS_2 ($0.159 \leq x \leq 0.325$) prepared in a chemical transport reaction [8]. The iron contents of the resulting powders were slightly lower than those of the starting mixtures. Powdered samples of Fe_xNbS_2 ($x=0.21$ and 0.30) displayed some super lattice reflections corresponding to the ideal compositions $x=1/4$ and $1/3$, respectively, as expected from the previous work [1–4]. The heat capacities of the samples were measured in the temperature range from 8 to 300 K with an adiabatic calorimeter at the Microcalorimetry Research Center in Osaka University. Each of the samples was loaded into the calorimeter vessel and sealed with He gas (100 kPa at room temperature) to assist quick thermal equilibration in the vessel. The mass of the $\text{Fe}_{0.14}\text{NbS}_2$ sample loaded into the vessel was 7.3075 g after buoyancy correction and those of the $\text{Fe}_{0.21}\text{NbS}_2$ and $\text{Fe}_{0.30}\text{NbS}_2$ samples were 6.8205 and 6.0985 g, respectively. Each sample contributed more than 20% to the total heat capacity at all temperatures. The working thermometers were platinum (Minco Products, S1055) and germanium (Lake-Shore Cryotronics, GR-200B-500) resistance thermometers and were used above and below 13.8 K, respectively. The temperature scales of both thermometers are based upon ITS-90. The operation and details of the adiabatic calorimeter were described elsewhere [9]. Magnetic susceptibility measurements on the samples (about 20 mg) were carried out by using a Quantum Design SQUID magnetometer in the Japan Advanced Institute of Science and Technology, Hokuriku, in the temperature range from 5 to 300 K and in a magnetic field of 100 Oe.

Results and discussion

The results of heat capacity and magnetic susceptibility measurements on the powdered sample of $\text{Fe}_{0.14}\text{NbS}_2$ are depicted in Fig. 1. It is seen that the temperature dependence of the magnetic susceptibility exhibits an anomaly as a shoulder at about 57 K, but no heat capacity anomaly is observed at this temperature, suggesting the existence of a spin-glass state. In order to confirm a spin-glass state, the magnetic

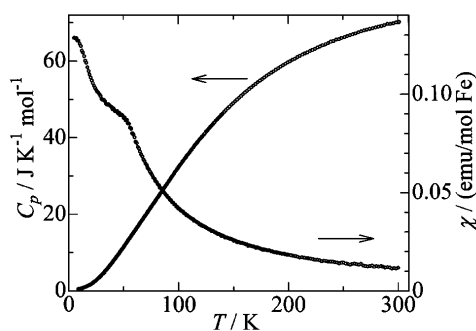


Fig. 1 Heat capacity (C_p) and magnetic susceptibility (χ) data for powdered $\text{Fe}_{0.14}\text{NbS}_2$ as functions of temperature

susceptibility data for this sample were derived from the FC and ZFC magnetizations in the applied magnetic field of 100 Oe. Figure 2 shows the temperature dependence of $\chi(\text{FC})$ and $\chi(\text{ZFC})$. There is a noteworthy difference between $\chi(\text{FC})$ and $\chi(\text{ZFC})$ at temperatures below 60 K, supporting the evidence of a spin-glass state at lower temperatures.

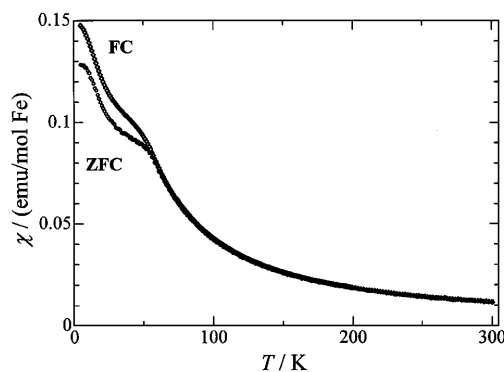


Fig. 2 Magnetic susceptibility (χ) data for powdered $\text{Fe}_{0.14}\text{NbS}_2$, derived from field-cooled (FC) and zero-field-cooled (ZFC) magnetizations measured with an applied magnetic field of 100 Oe, as functions of temperature

Figure 3 shows the heat capacity and the magnetic susceptibility data for the powdered sample of $\text{Fe}_{0.21}\text{NbS}_2$. There is a broad peak in the heat capacity at 100.5 ± 0.5 K, extending over a wide temperature range. The maximum in the magnetic susceptibility in Fig. 3 is seen at 105 ± 1 K, which is considerably lower than that ($T_N = 137$ K for $x = 1/4$) reported by Gorochov *et al.* [6], probably due to a strong composition dependence of the transition temperature near the composition $x = 1/4$. The heat capacity anomaly observed in this study is considered to be an antiferro-paramagnetic phase transition. It is clear from Fig. 3 that the magnetic susceptibility for powdered $\text{Fe}_{0.21}\text{NbS}_2$ increases with decreasing temperature. The present temperature dependence of the magnetic susceptibility for powdered $\text{Fe}_{0.21}\text{NbS}_2$ is similar to the sum of the magnetic susceptibilities, $(1/3)\chi_{\parallel} + (2/3)\chi_{\perp}$, for a single-crystal of $\text{Fe}_{1/4}\text{NbS}_2$ reported by Gorochov *et al.* [6], where χ_{\parallel} and χ_{\perp} are the magnetic sus-

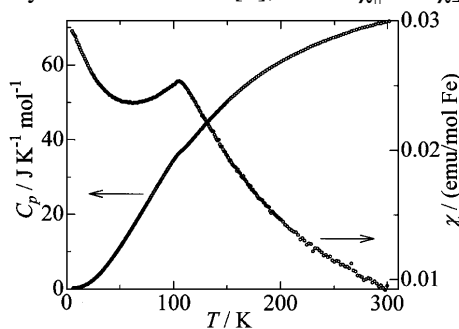


Fig. 3 Heat capacity (C_p) and magnetic susceptibility (χ) data for powdered $\text{Fe}_{0.21}\text{NbS}_2$ as functions of temperature

ceptibility contributions parallel to and perpendicular to the c -axis, respectively. Although this unusual behaviour at lower temperatures may be attributed to the temperature dependence of the magnetic susceptibility perpendicular to the c -axis, the reason is still open.

The results of heat capacity and magnetic susceptibility measurements on powdered $\text{Fe}_{0.30}\text{NbS}_2$ are given in Fig. 4, where a peak in the heat capacity and a maximum in the magnetic susceptibility are observed at 45.0 ± 0.5 and 40.5 ± 0.5 K, respectively. A spin glass for the composition $x=0.3$ is proposed by Doi and Tazuke [7], but spin ordering rather than spin glass occurs, since the heat capacity anomaly is observed in this study. The present heat capacity anomaly and the peak of magnetic susceptibility correspond to the antiferro-paramagnetic phase transition ($T_N=47$ K for $x=1/3$) reported by Friend *et al.* [5]. This phase transition seems to be of higher order, since the time necessary for thermal equilibration after an energy input was not prolonged near the transition temperature.

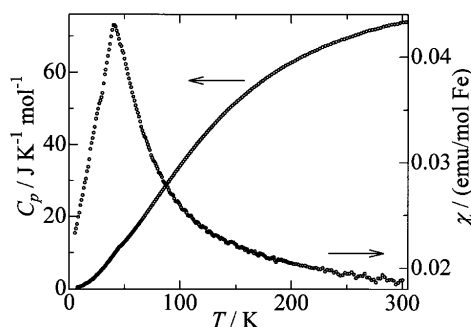


Fig. 4 Heat capacity (C_p) and magnetic susceptibility (χ) data for powdered $\text{Fe}_{0.30}\text{NbS}_2$ as functions of temperature

Figure 5 shows a plot of C_p/T vs. T for powdered Fe_xNbS_2 ($x=0.14, 0.21$ and 0.30) in order to clarify the composition dependence of the heat capacity at low temperatures. It is to be seen that the heat capacity data for $\text{Fe}_{0.30}\text{NbS}_2$ are larger than those for $\text{Fe}_{0.14}\text{NbS}_2$, since the constituent atomic numbers in the former are larger than those in the latter. However, it is unusual that the heat capacities for $\text{Fe}_{0.21}\text{NbS}_2$ at low temperatures are smaller than those for $\text{Fe}_{0.14}\text{NbS}_2$, although at high temperatures the former is larger than the latter due to the effect of the antiferro-paramagnetic transition at 100.5 K. This may be associated with the low-temperature spin-glass behaviour and/or the electric contribution to the heat capacity. It is to be noted that some of the heat capacity data for $\text{Fe}_{0.21}\text{NbS}_2$ at lower temperatures in Fig. 5 are somewhat high, but the reason is not clear.

In order to estimate the excess entropy due to the antiferro-paramagnetic phase transition for Fe_xNbS_2 ($x=0.21$ and 0.30), it is necessary to evaluate the baseline of the heat capacity. The equivalent Debye characteristic temperatures of the powdered Fe_xNbS_2 ($x=0.14, 0.21$ and 0.30), calculated from the heat capacity at each temperature in Figs 1, 3 and 4, are plotted in Fig. 6 as a function of temperature, on the assumption of three degrees of freedom per atom. The Debye characteristic tempera-

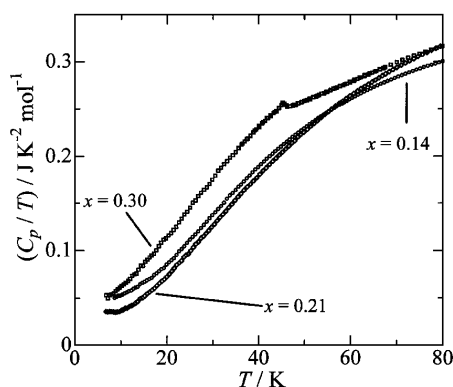


Fig. 5 Plots of C_p/T vs. T for powdered Fe_xNbS_2 ($x=0.14$, 0.21 and 0.30) to clarify the composition dependence of the heat capacity at low-temperature

tures for all samples agree well at temperatures above 130 K. However, at lower temperatures, the Debye characteristic temperatures for Fe_xNbS_2 ($x=0.14$ and 0.30) are lower than those for $\text{Fe}_{0.21}\text{NbS}_2$, while the Debye characteristic temperatures for Fe_xNbS_2 ($x=0.14$ and 0.30) are in good agreement above 90 K. We consider that the Debye characteristic temperatures for $\text{Fe}_{0.21}\text{NbS}_2$, which gives the highest Debye characteristic temperature for the three powdered samples below ~ 50 K, are suitable for use as the baseline of the heat capacity. These Debye characteristic temperatures at lower temperatures for $\text{Fe}_{0.21}\text{NbS}_2$ were smoothly extended to higher temperatures, as shown in the dotted curve in Fig. 6, and used for the baseline of the heat capacity for powdered Fe_xNbS_2 ($x=0.21$ and 0.30).

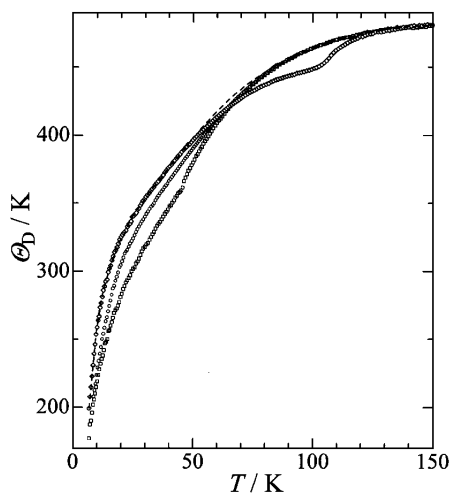


Fig. 6 Temperature dependence of the equivalent Debye characteristic temperatures (Θ_D) corresponding to the heat capacities measured for powdered Fe_xNbS_2 ($x=0.14$ (open circles), 0.21 (open diamonds) and 0.30 (open squares)) calculated by assuming three degrees of freedom per atom

Figures 7 and 8 present heat capacity data for $\text{Fe}_{0.21}\text{NbS}_2$ and $\text{Fe}_{0.30}\text{NbS}_2$, respectively, and their baselines are also depicted by the dotted curves. The excess entropies of the antiferro-paramagnetic phase transition for $\text{Fe}_{0.21}\text{NbS}_2$ and $\text{Fe}_{0.30}\text{NbS}_2$ were calculated to be 3.3 ± 0.1 and $6.9 \pm 0.1 \text{ J K}^{-1} (\text{mol Fe})^{-1}$, respectively. It is believed from the Mössbauer spectroscopy and magnetic susceptibility evidence that the iron exists in the high-spin state Fe^{2+} ($S=2$) [6, 7]. If this is the case, the theoretical transition entropy is calculated to be $R \ln(2S+1) = R \ln 5 = 13.4 \text{ J K}^{-1} (\text{mol Fe})^{-1}$. The experimental excess entropies of the antiferro-paramagnetic phase transition for Fe_xNbS_2 ($x=0.21$ and 0.30) amount to 25 and 52% of the theoretical value, respectively. The underestimate of the excess entropy is probably caused by overestimation of the baseline and/or an intrinsic residual entropy, owing to the frustration of spin in the antiferromagnetic triangular lattice [10]. However, it is still difficult to explain such a large difference. Another reason for the excess entropy may originate in the assumption of the high-spin state Fe^{2+} ($S=2$) in the present system. A spin state with an effectively smaller value of S may be one of the solutions to solve this problem, because it is suggested from the electrical conductivity and magnetic susceptibility measurements that some of the d electrons of iron ions are itinerant and the RKKY

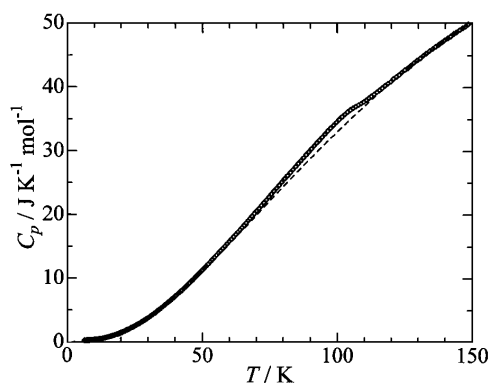


Fig. 7 Heat capacity data (C_p) and the baseline for $\text{Fe}_{0.21}\text{NbS}_2$ as functions of temperature

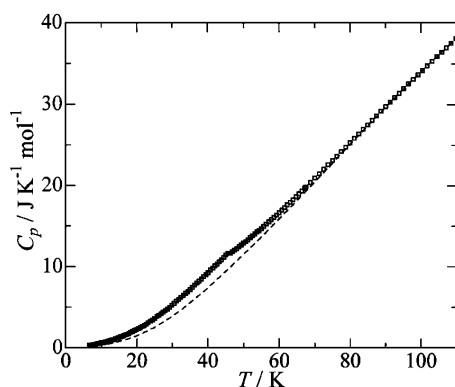


Fig. 8 Heat capacity data (C_p) and the baseline for $\text{Fe}_{0.30}\text{NbS}_2$ as functions of temperature

interaction is presumed to operate in these dilute iron compounds. In order to solve this problem more clearly, heat capacity and magnetic susceptibility measurements on single-crystals are necessary, and these are now in progress.

Conclusions

The heat capacities and magnetic susceptibilities of powdered samples of Fe_xNbS_2 ($x=0.14, 0.21$ and 0.30) were measured at temperatures from 8 to 303 K and from 5 to 300 K, respectively, with the following results:

1. For $\text{Fe}_{0.14}\text{NbS}_2$, the magnetic susceptibility exhibited an anomaly as a shoulder at about 57 K, and a marked difference between the field-cooled and the zero-field-cooled magnetizations was seen below 60 K, but no heat capacity anomaly was observed at this temperature. These facts indicate the existence of a spin-glass state for this concentration.

2. Anomalies in the heat capacity were observed for $\text{Fe}_{0.21}\text{NbS}_2$ and $\text{Fe}_{0.30}\text{NbS}_2$ at 100.5 and 45.0 K, respectively, where the magnetic susceptibility displayed a maximum, corresponding to an antiferro-paramagnetic phase transition.

3. The experimental excess entropies for the antiferro-paramagnetic phase transition were calculated to be 3.3 and $6.9 \text{ J K}^{-1} (\text{mol Fe})^{-1}$ for $\text{Fe}_{0.21}\text{NbS}_2$ and $\text{Fe}_{0.30}\text{NbS}_2$, respectively. These values do not agree with the theoretical value ($R \ln 5 = 13.4 \text{ J K}^{-1} (\text{mol Fe})^{-1}$) when the high-spin Fe^{2+} state is assumed, as observed in the Mössbauer study.

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