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Thermodynamic and magnetic properties of intercalated layered compounds Fe_xNbS_2

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Abstract

Heat capacities and magnetic susceptibilities of single crystals of Fe_xNbS_2 ($x=0.199$ and 0.239) were measured at temperatures from 1.8 to 300 K and from 5 to 300 K, respectively. For $Fe_{0.199}NbS_2$, anomalies in the heat capacity and magnetic susceptibility were observed at 36 and 39 K, respectively. A noteworthy difference between field-cooled $\chi_{\parallel}$ (FC) and zero field-cooled $\chi_{\parallel}$ (ZFC) below 60 K, supports the evidence of a spin-glass state for $Fe_{0.199}NbS_2$. An anomaly in the heat capacity was observed for $Fe_{0.239}NbS_2$ at 146.5 K, whereas the magnetic susceptibility displayed a maximum at 151 K, corresponding to an antiferro–paramagnetic phase transition. Heat capacity data of single crystal of $Fe_{0.239}NbS_2$ were in good agreement with those of powdered sample at temperatures excluding an order–disorder phase transition. The experimental excess entropy of antiferro–paramagnetic phase transition was calculated to be 8.4 J K^{-1} (mol Fe)$^{-1}$ for $Fe_{0.239}NbS_2$ and compared with the theoretical value calculated on the basis of entropy analysis.

Keywords: Heat capacity; Magnetic susceptibility; Intercalated compounds; Layered compounds; Fe_xNbS_2

1. Introduction

A number of transition metal dichalcogenides form intercalated layered compounds, and a weak van der Waals bonding between chalcogen atoms of adjacent layers allows easy intercalation of the metallic atoms. Among intercalated layered compounds, the iron atoms in Fe_xNbS_2 can occupy the vacant octahedral sites situated between the prismatic [S–Nb–S] layers, and form ordered super-lattices ($2a$ and c in $Fe_{1/4}NbS_2$; ($\sqrt{3}a$ and c in $Fe_{1/3}NbS_2$) related to the NbS_2-2*s* type [1,2].

The electrical and magnetic properties of Fe_xNbS_2 have been studied mainly for two compositions of $x=1/4$ and $1/3$ and these compounds have antiferro-magnetic orders below 137 and 47 K, respectively [3–6]. We measured the heat capacities and magnetic susceptibilities of powdered samples of Fe_xNbS_2 ($x=0.14$, 0.21 and 0.30) at temperatures ranging from 8 to 303 K and from 5 to 300 K, respectively [7]. For $Fe_{0.14}NbS_2$, 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. In this study, heat capacity and magnetic susceptibility of single crystals of Fe_xNbS_2 ($x=0.199$ and 0.239) were measured below 300 K as a function of temperature and compared with those of powder samples.

2. Experimental

Single crystals of Fe_xNbS_2 ($x=0.199$ and 0.239) were grown by a chemical transport reaction using iodine as a transport agent. The iron contents, x, were determined by an electron probe micro-analyzer. The electron diffraction patterns of the sample at characteristic content $x=0.239$ show the $2a\times2a$ superstructure.

Heat capacity measurement was carried out by using PPMS (Quantum Design) in the temperature range from 1.8 to 300 K; the sample weights were 2.243 mg for $x=0.199$ and 0.867 mg for $x=0.239$. Magnetic susceptibility was measured by a static-field of a SQUID magnetometer in the temperature range 5–300 K. The mag-

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netic field was applied in parallel to the *c*-axis of the stacked crystals; sample weights were 10–20 mg. These experiments were carried out by using samples picked up from the sample bath, because the quality of crystal depends on synthetic conditions. The magnetic susceptibility data for these single crystals were derived from zero field cooling (ZFC) and the field cooling (FC) experiments with the applied magnetic field of 100 Oe in order to confirm a spin-glass state.

3. Results and discussion

The results of heat capacity and magnetic susceptibility measurements on a single crystal of $Fe_{0.199}NbS_2$ are depicted in Fig. 1. Magnetic susceptibility data ($\chi_{\|}$) parallel to the *c*-axis are derived from field-cooled $\chi_{\|}$(FC) and zero field-cooled $\chi_{\|}$(ZFC) magnetizations measured with an applied magnetic field of 100 Oe. An anomaly in the magnetic susceptibility is seen at 39 K, whereas a small anomaly in the heat capacity is also observed at 36±1 K. A noteworthy difference between $\chi_{\|}$(FC) and $\chi_{\|}$(ZFC) is seen at temperatures below 60 K, supporting the evidence of a spin-glass at lower temperature.

Fig. 2 shows the heat capacity and the magnetic susceptibility data for a single crystal of $Fe_{0.239}NbS_2$ ($x \sim 1/4$) having $2a \times 2a$ superstructure. A sharp λ-type peak in the heat capacity was clearly observed for the first time at 146.5±1.0 K, in spite of the small amount of the sample (0.867 mg) used in this study. A maximum in the magnetic susceptibility is also seen at 151 K, which is a slightly higher than that of $T_N = 137$ K for $x = 1/4$ reported by Gorochov et al. [4], due to a strong composition dependence of the transition temperature near the composition $x = 1/4$ [6]. The present heat capacity anomaly observed in this study is considered to be antiferro–paramagnetic phase transition. As seen in Fig. 2, there is a difference between $\chi_{\|}$(FC) and $\chi_{\|}$(ZFC) below 150 K, supporting the evidence of a magnetic disorder in the superstructure. The present temperature dependence of the magnetic susceptibility in parallel to the *c*-axis ($\chi_{\|}$) for $Fe_{0.239}NbS_2$ single crystal is similar to that for $Fe_{1/4}NbS_2$ single crystal reported by Gorochov et al. [4], but the reason of unusual behavior at lower temperature is still open.

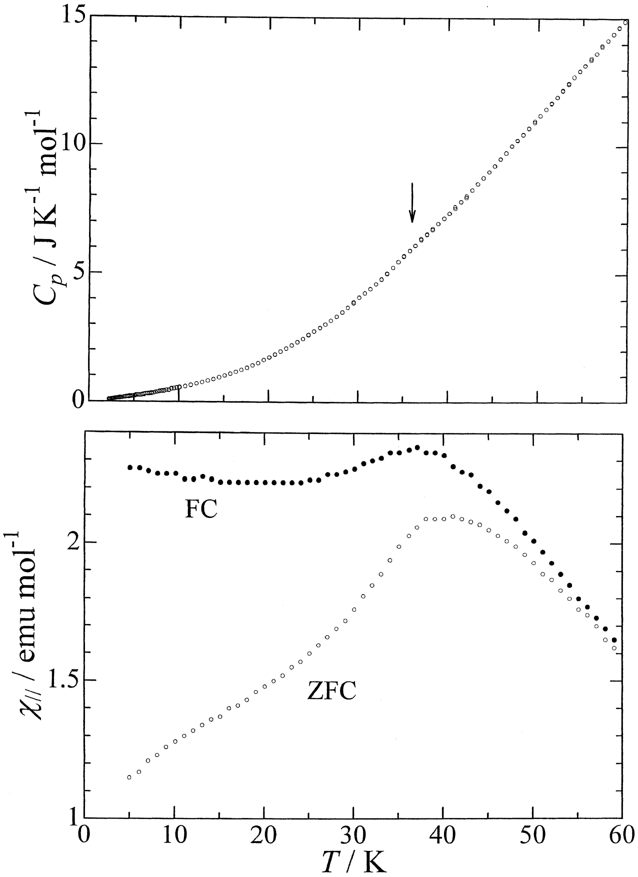

Fig. 1. Heat capacity (C_p) and magnetic susceptibility ($\chi_{\|}$) data for a single crystal of $Fe_{0.199}NbS_2$ as a function of temperature. The $\chi_{\|}$ values parallel to the *c*-axis are derived from field-cooled $\chi_{\|}$(FC) (●) and zero field-cooled $\chi_{\|}$(ZFC) (○) magnetizations measured with an applied magnetic field of 100 Oe.

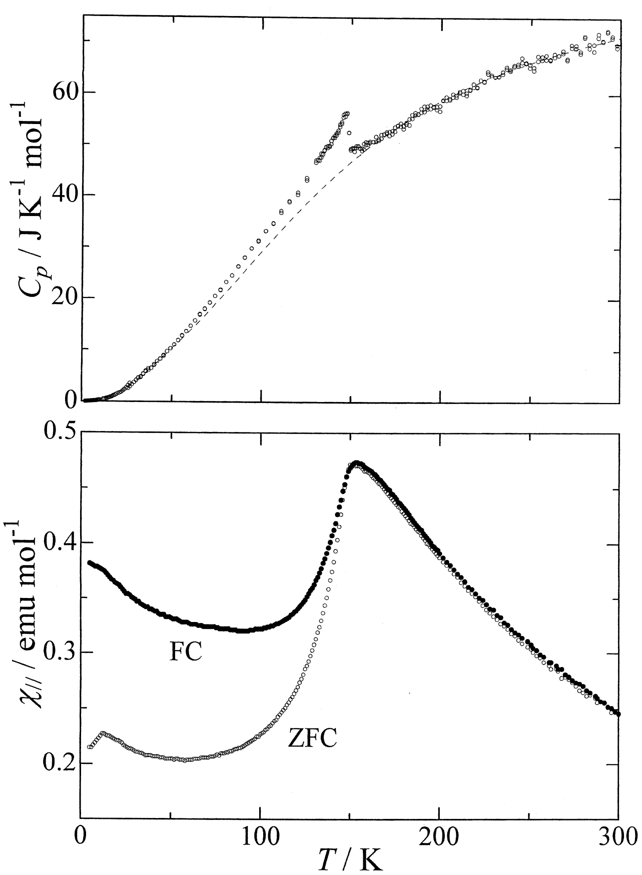

Fig. 2. Heat capacity (C_p) and magnetic susceptibility ($\chi_{\|}$) data for a single crystal of $Fe_{0.239}NbS_2$ as a function of temperature. The $\chi_{\|}$ values parallel to the *c*-axis are derived from field-cooled $\chi_{\|}$(FC) (●) and zero field-cooled $\chi_{\|}$(ZFC) (○) magnetizations measured with an applied magnetic field of 100 Oe.

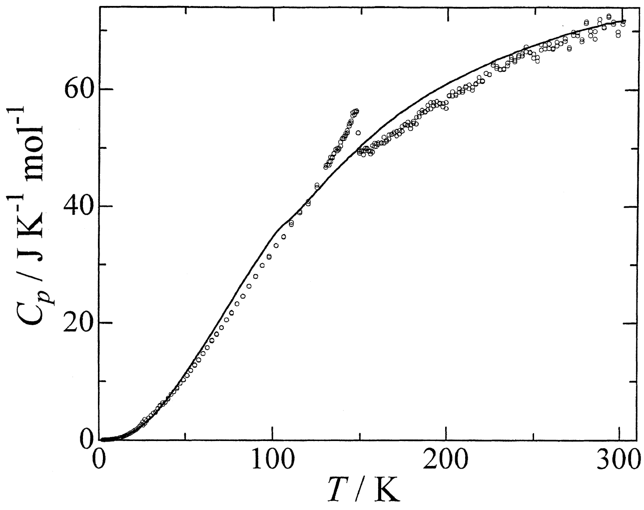

Fig. 3. Heat capacity data of $Fe_{0.239}NbS_2$ single crystal together with those of $Fe_{0.21}NbS_2$ powdered sample (—) as a function of temperature.

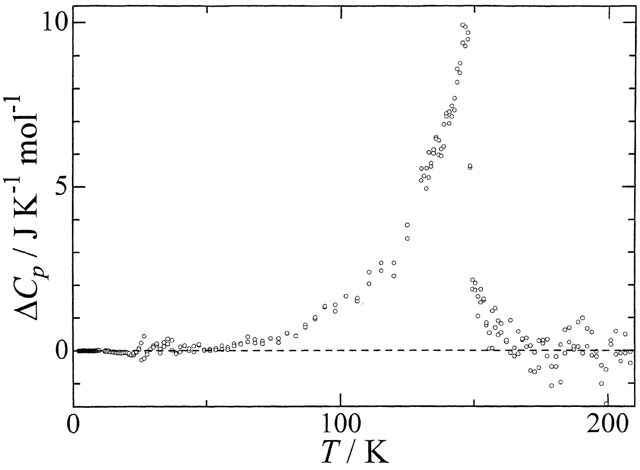

Fig. 4. Excess heat capacity of a single crystal of $Fe_{0.239}NbS_2$ as a function of temperature.

Fig. 3 shows the heat capacity data of a single crystal of $Fe_{0.239}NbS_2$ together with those of powdered sample of $Fe_{0.21}NbS_2$. A sharp λ-type heat capacity for $Fe_{0.239}NbS_2$ single crystal is clearly seen at 146.5 K, whereas a broad peak is observed at 100.5 K for $Fe_{0.21}NbS_2$ powdered sample. A broad peak of powdered sample may be caused by slightly different compositions in the sample. The difference of the transition temperature between a single crystal and powdered sample is probably caused by a strong composition dependence of the transition temperature near the composition $x=1/4$. As seen in Fig. 3, heat capacity data of a single crystal are in good agreement with those of powdered sample at temperatures below 40 K and above 280 K.

The base line of the heat capacity is depicted by the dotted curve as seen in Fig. 2. The excess heat capacities due to the antiferro–paramagnetic phase transition for $Fe_{0.239}NbS_2$ (x~1/4) are calculated from Fig. 2, and the results are shown in Fig. 4 as a function of temperature. The excess entropy of the antiferro–paramagnetic phase transition for $Fe_{0.239}NbS_2$ was calculated to be 8.4 J K^{-1} (mol Fe)$^{-1}$. It is believed from Mössbauer spectroscopy and magnetic susceptibility data that the iron exists in the high-spin state Fe^{2+}($S=2$) [4,5]. In this case, the theoretical transition entropy is calculated to be $R\ln(2S+1)=R\ln 5=13.4$ J K^{-1} (mol Fe)$^{-1}$. The experimental excess entropy of the antiferro–paramagnetic phase transition amounts to 63% of the theoretical value. The underestimate of the excess entropy is probably caused by the intrinsic residual entropy, owing to the frustration of spin in the antiferro-magnetic triangular lattice [8]. Another reason for the excess entropy difference between theoretical and experimental values may originate in the assumption of the high-spin state Fe^{2+} ($S=2$) in the present system. A spin state with an effective smaller S value 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 interaction is presumed to operate in these dilute iron compounds.

4. Conclusions

The heat capacities and magnetic susceptibilities of Fe_xNbS_2 ($x=0.199$ and 0.239) single crystals were measured at temperatures from 1.8 to 300 K and from 5 to 300 K, respectively, and the following results are derived:

(1) For $Fe_{0.199}NbS_2$ single crystal, anomalies in the heat capacity and magnetic susceptibility were observed at 36 and 39 K, respectively. A noteworthy difference between $\chi_{\|}$(FC) and $\chi_{\|}$(ZFC) was observed at temperatures below 60 K, supporting the evidence of a spin-glass state at lower temperature.

(2) A sharp λ-type anomaly in the heat capacity was observed for the first time for $Fe_{0.239}NbS_2$ single crystal at 146.5 K, whereas the magnetic susceptibility displayed a maximum at 151 K, corresponding to an antiferro-paramagnetic phase transition. The heat capacity data of a single crystal of $Fe_{0.239}NbS_2$ were in good agreement with those of powdered sample of $Fe_{0.21}NbS_2$ at temperatures below 40 K and above 280 K.

(3) The experimental excess entropy for antiferro-paramagnetic phase transition was calculated to be 8.4 J K^{-1} (mol Fe)$^{-1}$ for $Fe_{0.239}NbS_2$ single crystal and compared with the theoretical value calculated on the basis of entropy analysis.

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