

Magnetic and electrical properties of NdNiSn

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Abstract

Magnetization and resistivity measurements have been carried out on the equiatomic ternary compound NdNiSn in the temperature range 2–200K. The compound crystallizes in the orthorhombic CeNiSn-type structure with space group Pna2₁. Magnetic susceptibility shows a distinct feature at $T_N = 3$ K (Néel temperature), typical of a phase transition from an antiferromagnetic to paramagnetic state. In the paramagnetic regime, the magnetic susceptibility obeys Curie-Weiss behavior yielding an effective magnetic moment $\mu_{eff} = 3.32 \mu_B$ at lower temperatures, and $3.88 \mu_B$ at higher temperatures. The reduction in the magnetic moment at lower temperatures is attributed to a crystalline electric field (CEF) effect, while the slight excess of magnetic moment at high temperatures compared to that of the free Nd³⁺ ion ($3.62 \mu_B$) indicates that only a very small magnetic moment, at most $0.3 \mu_B$, is induced at the Ni sites. The electrical resistivity exhibits metallic behavior and no anomaly is observed at the respective Néel temperature. Analysis of the resistivity data in terms of crystalline electric fields including *s-d* electron scattering reveals that the ground magnetic state for the Nd³⁺ ions is a doublet of $J = \pm 5/2$ states, with a first excited doublet of $J = \pm 7/2$ states having an energy splitting of 56 K, with the next excited multiplet 139 K above the ground levels. These results are in fairly good agreement with those reported in the literature based on magnetic susceptibility and heat capacity measurements.

Key words: Intermetallics Compounds, Magnetic Measurements, Electrical Resistivity, CEF effects

PACS: 71.20.Eh, 71.70.-d, 75.10.Dg, 74.25.-q

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1 Introduction

NdNiSn is a member of a large family of ternary compounds with the general chemical formula RTX (R = rare-earth, T = transition metal and X = p -element) [1–3]. These materials are still a subject of intensive study because of the interesting physical properties some of them exhibit, such as the Kondo effect, superconductivity, spin fluctuations, valence instabilities and heavy Fermion behavior. The substitution of one transition metal and/or one rare earth for another in this family changes the hybridization strength between the $4f$ states and the conduction electrons, thereby giving rise to interesting effects due to competition between intrasite Kondo effect and intersite Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. For example, CeNiSn is well-known as a Kondo-type compound [4,5], a compensated semiconductor with a pseudo-gap at low temperatures, whereas NdNiSn exhibits metallic-like behavior, ordering antiferromagnetically with a Néel temperature (T_N) of approximately 3 K. Recent works have reported results of crystal structure, magnetic susceptibility, heat capacity [6], X-ray photoemission spectroscopy [3], neutron diffraction [7] and Mössbauer [8] studies on NdNiSn, but there are no reported resistivity measurements on this compound, to our best knowledge. In this paper, we report the results of resistivity measurements as well as magnetic measurements for NdNiSn. The resistivity analysis reveals that the crystal-field-split ground state of the Nd^{3+} ion is a doublet $J = \pm 5/2$, and the first excited state a doublet $J = \pm 7/2$ with energy splitting of 56 K, while the second excited states are composed of $J = \pm 1/2$, $\pm 3/2$, and $\pm 9/2$ with energy splitting of 139 K. Our magnetization measurements and resistivity results are found to be in fairly good agreement with the previously reported studies in the literature.

2 Experimental

The NdNiSn compound was prepared by arc melting under argon atmosphere from starting materials of 99.9% purity. The ingot was remelted several times. The as-cast structure was analyzed by X-ray diffraction using $\text{Cu K}\alpha$ radiation. The sample is not entirely single phase, but contains a secondary phase about less than 10%. The main phase is crystalized in orthorhombic symmetry with space group $\text{Pna}2_1$ (CeNiSn type). The lattice constants are found to be $a = 7.535 \text{ \AA}$, $b = 4.585 \text{ \AA}$ and $c = 7.590 \text{ \AA}$. This structure is similar to that of ϵ -TiNiSi [9].

A SQUID magnetometer was used to measure the DC magnetization in the temperature range of 2–200K in the presence of magnetic fields up to 70 kOe. The magnetic field was applied along the long side of the sample in order

to reduce the demagnetization fields. AC susceptibility measurements were performed using a commercial Lake-Shore AC susceptometer ($f = 133.3$ Hz, $H = 1$ mT) in the temperature range 100–300 K.

Resistivity of the samples was measured with a standard DC four-probe set-up over a 2–300 K temperature range. A calibrated Ge resistance thermometer (GR-200A-2500) was used to measure the temperature below 80 K. For higher temperatures, a calibrated Pt thermometer was used. Electrical contacts were made using silver paint and 25 μm gold wire.

3 Results and discussion

3.1 Magnetization measurements

$M(T)$ was measured in an external field of $H = 100$ Oe, from which M/H is plotted in Fig. 1. A distinct feature was observed in $M(T)/H$ at about 3 K due to the transition from a paramagnetic state to an antiferromagnetic state (Néel temperature = T_N). The inset to this figure shows $M(T)/H$ in an external field of $H = 10$ Oe for both zero-field cooled (ZFC) and field-cooled (FC) cases. As seen in the figure, the FC and ZFC curves are retraceable. Above $T = T_N$ the susceptibility ($\chi = M/H$) follows a Curie-Weiss type behavior. We fit to the Curie-Weiss law

$$\chi = \chi_0 + \frac{C_M}{T - \Theta_{CW}}, \quad (1)$$

to the data in the temperature range 10–200 K. Here C_M is the Curie constant and Θ_{CW} is the paramagnetic Curie temperature. The parameters obtained are an effective moment $\mu_{eff}^{low} = 3.32\mu_B$ and a Curie-Weiss temperature $\Theta_{CW} = -2.35$ K, indicating that the magnetic correlations in the temperature range of the fit are antiferromagnetic, and a temperature-independent susceptibility $\chi_0 = 2 \times 10^{-3}$ emu/mole. The observed value for μ_{eff} at lower temperatures is smaller than that of the free Nd^{3+} ion suggesting that the reduction in μ_{eff} is directly related to CEF level splitting and f -conduction electron hybridization. Fig. 2 shows the high-temperature (100–300 K) AC magnetic susceptibility of NdNiSn. This also follows a Curie-Weiss law, with an effective moment $\mu_{eff}^{high} = 3.88 \mu_B$, $\Theta_{CW} = -20$ K and $\chi_0 = -3 \times 10^{-3}$ emu/mole. The observed effective moment at higher temperatures is somewhat larger than the free Nd value of $3.62 \mu_B$. This could be ascribed to an induced magnetic moment of the Ni atoms (at most $0.3 \mu_B$).

Magnetization as a function of magnetic field up to 70 kOe for some selected temperatures are shown in Fig. 3. The lowest-temperature measurement was done at 2 K, below T_N (3 K as indicated by the susceptibility). An additional curve was obtained at $T = T_N$, while the remaining data for 35 K and 200 K lie above T_N . It should be noted that M vs. H at $T = 2$ K exhibits an abrupt change at $H = 8$ kOe. A similar observation was made on the same compound in earlier report [10]. However, it is not clear whether this is a metamagnetic transition or not. It has already been reported that NdNiSn has an incommensurate sine-wave modulated spin structure, from neutron diffraction measurements [7]. As an alternative suggestion, one can ascribe this to re-orientation of spin structure in order to minimize both anisotropy and exchange interactions between Nd moments.

It has been customary to plot M against $1/H$ and extrapolate to $1/H = 0$ to obtain the saturation magnetization value. But Kouvel and Graham [11] showed that extrapolation versus $\frac{1}{\sqrt{H}}$ gave better straight lines. Even though it is not clear that this conclusion is valid for very high fields, we have used an expression of the following form: $M = M_s - a/\sqrt{H}$. Indeed, we get an excellent linear fit for M vs. $1/\sqrt{H}$ for high magnetic fields. From the best fitting to the magnetization data, the saturation magnetic moments are found to be $2.21 \mu_B/\text{f.u.}$ for $T = 2$ K. Considering that only Nd atoms contribute to the magnetization, the estimated moment is smaller than that of free Nd^{3+} ions ($gJ = 3.27 \mu_B$). However, the resistivity analysis based on CEF-split levels, given below, indicates that a $J = \pm 5/2$ doublet is the ground state. Using the Landé g factor for the free Nd^{3+} ion, $g = 8/11$ yields $gJ = 1.82 \mu_B$. We have estimated $0.3 \mu_B$ at most for localized Ni d -electrons by means of AC-susceptibility data. All these results lead us to suggest that a small magnetic moment also forms on the Ni atom-site.

3.2 Electrical resistivity analysis

The resistivity was measured as a function of temperature in the range 2–160 K as given in Figure 4. Linear temperature dependence is the dominant behavior for temperatures above $T = 100$ K. This linear dependence is likely due to electron-phonon scattering and can be described by a Bloch-Grüneisen equation. Below $T = 100$ K, the resistivity has a downward concave form. This type of behavior is characteristic of most intermetallic ternary alloys presumably due to CEF effects. The temperature dependence of the resistivity in the covered temperature region can be well described using different mechanisms as follows:

$$\rho(T) = \rho_0 + \rho_{sf}(T) + \rho_{sd}(T) + \rho_{ph}(T) \quad (2)$$

where ρ_0 is the temperature independent residual resistivity, the second term describes the effect of localized f -magnetic moments on the resistivity due to exchange scattering between s -electrons and localized f -electrons in the presence of a crystal field. The third term presents a quadratic temperature dependence (T^2 -term) associated with the small magnetic moments of Ni in the compound, due to s - d scattering. This contribution has been derived by Kasuya [12] and by Goodings [13]. The last term denotes the electron-phonon contribution which is non-magnetic in origin. We have evaluated it separately by using the following Bloch-Grüneisen relation

$$\rho_{ph} = \rho_{os} + 4RT(T/T_D)^4 J_5(T_D/T) \quad (3)$$

where T_D is the Debye temperature, $J_5(T_D/T)$ is the Grüneisen function, for which R refers to the linear dependence at high temperature, and ρ_{os} is the residual resistivity. The best fit to the data in the temperature range 80–150 K is shown in Fig. 4 by a continuous line. The fitting parameters are $\rho_0 = 23.2 \mu\Omega \text{ cm}$, $R = 1.08 \mu\Omega \text{ cm/K}$ and $T_D = 202 \text{ K}$, which seems to be reasonable when compared to those of isoelectronic similar compounds.

In order to better examine the magnetic contribution to the resistivity by the mechanisms mentioned above, the temperature derivative of the magnetic part remaining after subtracting the non-magnetic ρ_{ph} from the observed resistivity $\rho(T)$ is plotted in Fig. 5. We assume that the CEF mechanism, being associated with a spin-disorder effect, is predominant over other possible mechanisms. In order to analyze the experimental data on the basis of CEF splitting, we used the following expression [14,15] for this part of the resistivity:

$$\begin{aligned} \rho_{sf}(T) = & \frac{3\pi N m}{\hbar e^2 E_F} G^2 (g-1)^2 \\ & \times \sum_{m_s, m_{s'}, i, i'} \langle m_{s'}, i' | \mathbf{s} \cdot \mathbf{J} | m_s, i \rangle^2 p_i f_{ii'}, \end{aligned} \quad (4)$$

where m_s and $m_{s'}$ are the spins of the conduction electrons in the initial and final states. The $f_{ii'}$ in the equation are given by

$$f_{ii'} = \frac{2}{1 + \exp(-E_{ii'}/k_B T)}, \quad (5)$$

where $E_{ii'}$ is the energy difference between states i and i' . The probability p_i that an electron in a crystal-field is in state i with the energy E_i is given by the Boltzmann relation:

$$p_i = \frac{N_i}{N} = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}. \quad (6)$$

Note that the sum should be taken over all crystal field states. To determine the CEF scheme, we have adapted the CEF scheme for Nd^{3+} in a orthorhombic environment consisting of the 10-fold degeneracy lifted into five Kramers doublets. This scheme was confirmed in previous reports by means of susceptibility and heat capacity measurements [6]. There are a number of ways to make an assignment for ground and excited levels. Keeping in mind the estimated spontaneous magnetic moment of this sample ($\sim 2.21 \mu_B$), it seems likely that the ground state consists of $J = \pm 5/2$. However, there are also two alternatives to our assignment of the ground levels: $J = \pm 1/2$ and $J = \pm 3/2$. Considering the $\Delta J_z = \pm 1$ selection rule, the first excited states are estimated to be $J = \pm 7/2$ for the most likely scheme and $J = \pm 3/2$ and $J = \pm 5/2$, respectively for the other alternatives. For simplicity, we assume that the ground state is a $J = \pm 5/2$ doublet, the first excited state is a $J = \pm 7/2$ doublet, and the other remaining levels are 6-fold degenerate set of second-excited levels. Using Eqs. 4, 5, and 6 we obtained the following expression:

$$\rho_{sf} = \frac{3\pi Nm}{\hbar e^2 E_F} G^2 (g-1)^2 p_i (6.25 + 12.25x + 31.875y + 8.0 \frac{x}{x+1} + 10.5 \frac{y}{1+y} + 4.5 \frac{xy}{x+y}), \quad (7)$$

where $x = \exp(-\Delta_1/T)$, $y = \exp(-\Delta_2/T)$ and $p_i = \frac{1}{1+x+3y}$. Δ_1 is the splitting energy between the ground state doublet and the first excited doublet, while Δ_2 is the separation between the ground state and the second 6-fold degenerate states. It can be seen that at lower temperatures (compared to those of the splitting energy values, Δ_1 and Δ_2), namely as $x \rightarrow 1$ and $y \rightarrow 1$, the above equation becomes identical to the value of ρ_{sf}^0 with $J = 9/2$. For the other alternative cases, we have obtained similar expressions (not shown here). The temperature derivative of the magnetic part of $\rho(T)$ as described above is fitted to the temperature derivative of ρ_{sf} plus a linear temperature term, aT (a is the fitting parameter) arising from s - d electron scattering. The best fit was obtained for our proposed CEF level scheme as opposed to the two suggested to be alternative. The continuous line in Fig. 5 represents the theoretical values obtained for the ground level as a $J = \pm 5/2$ doublet, the first excited state as a $J = \pm 7/2$ doublet and the second excited states 6-fold degenerate $J = \pm 9/2$, $\pm 3/2$, and $\pm 1/2$. The fitting parameters are: $\Delta_1 = 56$ K, $\Delta_2 = 139$ K, $a = 1.05 \times 10^{-5} \mu\Omega \text{ cm/K}^2$. However, as alternative assignments of the CEF, we also use the CEF-scheme having a ground-level $\pm 5/2$ doublet, a first excited quartet $\pm 3/2$ and $\pm 7/2$, and a second excited quartet $\pm 1/2$ and $\pm 9/2$. For this case, using Eqs. 4, 5, and 6 we obtained the following expression:

$$\rho_{sf} = \frac{3\pi Nm}{\hbar e^2 E_F} G^2 (g-1)^2 p_i (6.25 + 14.5x$$

$$+23.625y + 18.5\frac{x}{x+1} + 16.5\frac{xy}{x+y}). \quad (8)$$

Here, the fitting parameters are: $\Delta_1 = 68$ K, $\Delta_2 = 156$ K, $a = 5.374 \times 10^{-6}$ $\mu\Omega$ cm/K². However, the fitting for this scheme seems to be relatively poor (see dashed curve in Fig.5).

The distinct feature observed at $T = 3$ K in the magnetic susceptibility and the heat capacity [6] (indicating a transition from a PM state to AFM state, known as a Néel temperature) does not show up in the resistivity data. The resistivity of this sample at lower temperatures is about 10 $\mu\Omega$ cm. The mean free path of the conduction electrons can be estimated to be a few hundred Å. According to the arguments of Fisher and Langer [16], localized spins will not scatter the electrons coherently unless the correlation length is comparable to the electron mean free path, λ_{mfp} . They also asserted that a wide variety of resistive anomalies, which are known to occur in rare earth metals (first order phase transition, and other magnetic phase transitions) manifest themselves as a dominant contribution to the temperature-dependent part of the resistivity provided that λ_{mfp} is comparable to the mean magnetic correlation length, ζ .

4 Conclusions

Magnetization, AC and DC magnetic susceptibilities, and electrical resistivity measurements have been carried out on NdNiSn. The temperature dependence of the magnetization exhibits a distinct feature of a typical phase transition from an antiferromagnetic to a paramagnetic state at 3 K (Néel temperature). AC susceptibility analysis indicates that besides the Nd magnetic moment due to localized 4*f*-electrons, a very small magnetic moment (at most $0.3\mu_B$) also occurs at the Ni site, presumably due to the polarized Ni 3*d*-electron states hybridizing with the Nd 5*d*-electron states. This observation was also confirmed by the resistivity analysis by taking the *s-d* electron scattering mechanism into account. CEF effects manifest themselves in both susceptibility and resistivity. Resistivity data were described well using a Bloch-Grüneisen expression for the electron-phonon contribution, T^2 behavior for *s-d* electron scattering and a general expression given in the literature for *s*-conduction electrons and *f*-localized states lifted by crystalline electric fields. A possible CEF scheme was obtained for NdNiSn from the resistivity data. To determine the CEF scheme, we adopted five Kramers doublets split by a CEF [6,7]. After making best-fitting attempts for the possible alternative cases, we obtained a best fit for the case that $J = \pm 5/2$ is the ground state, $J = \pm 7/2$ is the first excited state, and the next excited multiplet consist of the remaining doublets. Best fitting parameters are $\Delta_1 = 56$ K and $\Delta_2 = 139$ K, which are in fairly good agreement with earlier reports [6,7]

5 Acknowledgments

This work was supported by TUBITAK through Project No: TBAG-2219(102T112) and by the Robert A. Welch Foundation (grant A-1526).

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6 Figure Captions

Fig. 1 Low-field DC magnetic susceptibility (M/H) vs. temperature (T) for a measuring field of 100 Oe. Open circles: data taken during sample cooling in the measuring field. Solid curve: theoretical fit to Curie-Weiss expression. Inset shows low-field DC susceptibility with a measuring field of 10 Oe, for both ZFC and FC cases. Note that there are no irreversibility effects.

Fig. 2 Temperature dependence of AC susceptibility in the range $10K \leq T \leq 300K$. The theoretical fit is given by the solid curve.

Fig. 3 Magnetization (M) versus external magnetic field(H) up to 70 kOe for selected temperatures below 200 K.

Fig. 4 Resistivity vs. temperature measured in the range 2–160 K. Bloch-Grüneisen fit given by the solid curve. Inset shows resistivity as a function of temperature to emphasize that no anomaly is observed at the Néel temperature, $T_N = 3$ K.

Fig. 5 Temperature derivative of magnetic part of the resistivity. Solid curve: best fit using the expression described in the text, Eq. 7, labeled Fit1, for the CEF scheme indicated schematically on the figure. The alternative assignment (Eq. 8, as described in the text) provides the best fitting depicted by the dashed curve, labeled Fit2.









