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$Ce_2Ni_3Si_5$: A mixed-valence cerium compound

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The results of electrical resistivity (4.2–300 K), magnetic susceptibility (5–300 K) and specific heat (2–20 K) are reported on the ternary orthorhombic rare-earth compound $Ce_2Ni_3Si_5$. The resistivity of the material is nearly temperature independent above 120 K unlike that of a normal metallic material. The magnetic contribution to resistivity shows a broad maximum around 200 K. At low temperatures, the resistivity follows a T^2 behavior in the temperature range 4–13 K. The inverse magnetic susceptibility deviates from Curie-Weiss behavior below 80 K where it exhibits a broad maximum in the χ vs T curve. Specific heat measurements (2–20 K) give a value of $\gamma \approx 62$ mJ/Ce mol K^2 which is similar in magnitude to those encountered in valence-fluctuating systems. From these observations we conclude that $Ce_2Ni_3Si_5$ is a Ce-based valence-fluctuation compound.

I. INTRODUCTION

Physical properties of f electron elements in their compounds and intermetallics have always been fascinating for more than one reason. Quite a few compounds containing these elements exhibit anomalous properties due to the proximity of the $4f$ level of the ion to the Fermi level of the system.[1,2] Some of these anomalous properties are Kondo-type behavior in concentrated systems, high magnetic ordering temperature, heavy fermion behavior,[3] etc. Notable among them is the property of valence-fluctuating behavior (VF) of Eu,[4] Yb,[5] and Ce,[6,7] along with its heavy fermion behavior.[3] The hybridization of $4f$ shell with conduction electrons is believed to give rise to these anomalous properties. The study of Ce-based compounds is of particular interest as in this case the $4f$ shell contains just one electron, which may help us to explain this system with relative ease, as intra-$4f$ electron interactions can be ignored. In this paper we report the study of physical properties, viz., dc magnetic susceptibility, resistivity, and specific heat of a Ce-based ternary compound $Ce_2Ni_3Si_5$. We had identified earlier Eu to be a valence-fluctuating state in $Eu_2Ni_3Si_5$.[8] Often, the Ce analog of a Eu-based valence-fluctuating compound is found to exhibit valence fluctuation and related anomalous physical properties. This is an additional motivation for studying $Ce_2Ni_3Si_5$. Although the synthesis of $Ce_2Ni_3Si_5$ was reported earlier,[9] to the best of our knowledge there is no report on the physical properties of this compound. From our measurements we show that Ce ion is in a mixed-valence state in this compound.

II. EXPERIMENTAL

The compound $Ce_2Ni_3Si_5$ was prepared by arc melting together the stoichiometric amounts of the constituent elements of purity better than 99.95% on a water-cooled copper hearth under argon atmosphere. For comparison the nonmagnetic analog $Y_2Ni_3Si_5$, was also synthesized. The materials were annealed at 1100 °C for one day and at 1000 °C for 7 days. The materials were characterized at room temperature by powder x-ray diffraction technique using Cu $K\alpha$ radiation in a commercial (Jeol, Japan) diffractometer.

Magnetic susceptibility studies were performed in the temperature range 5–300 K in an applied magnetic field of 4000 Gauss using commercial SQUID magnetometer (Quantum Design Inc., USA).

Electrical resistivity in the temperature range 4.2–300 K was measured using a standard four-probe dc method employing a home-built set-up. The electrical contacts to the samples were made with silver wires with the help of conducting silver paint. Temperature was measured using a calibrated silicon diode. Long bar-shaped samples (size 8 mm × 5 mm × 1.5 mm approx) of $Ce_2Ni_3Si_5$ and $Y_2Ni_3Si_5$ were used for the measurements and data were collected by applying the current in forward and reverse directions and the average was taken to avoid errors due to thermo emf. Resistivity of $Y_2Ni_3Si_5$ was measured to estimate the phonon contribution to the resistivity. $La_2Ni_3Si_5$ would have probably been more appropriate as its lattice dimensions would be closer to that of Ce compound, but we were not successful in forming single-phase $La_2Ni_3Si_5$.

The specific heat (2–20 K) was measured using a home-built set-up employing semi-adiabatic heat pulse method. A calibrated germanium resistance thermometer was used to measure the temperature.

III. RESULTS AND DISCUSSION

The room-temperature powder x-ray diffraction pattern confirmed the formation of single-phase materials of

$Ce_2Ni_3Si_5$ and $Y_2Ni_3Si_5$ in the orthorhombic $U_2Co_3Si_5$ crystal structure type (space group *Ibam*) consistent with earlier reports.[9] It is pertinent to note that in this structure rare earth occupies only one type of site, viz., the $8j$ position. The other two ions occupy different distinct sites: Ni(1) atom occupies $8j$ position, Ni(2) atom occupies $4b$ position, Si(1) atoms occupy $8j$ sites, Si(2) atoms in $8g$ positions, and Si(3) atoms occupy $4a$ positions. This arrangement gives four formula units per unit cell. It may be noted that $8j$ positions of different elements have different values of x and y (the value of z being 0 for all of them). The lattice parameters obtained at room temperature are $a = 9.639$ Å, $b = 11.402$ Å, $c = 5.754$ Å, for $Ce_2Ni_3Si_5$ and $a = 9.540$ Å, $b = 11.092$ Å, $c = 5.628$ Å for $Y_2Ni_3Si_5$ which are in reasonable agreement with that reported in the literature.[9]

The striking feature of resistivity (Fig. 1), $\rho(T)$, of $Ce_2Ni_3Si_5$ is its remarkable temperature dependence. It is nearly constant in the high-temperature region (between 120–300 K) while the resistivity of the nonmagnetic $Y_2Ni_3Si_5$ exhibits the usual metallic behavior and has a nearly linear temperature dependence in this temperature region. After subtracting the phonon contribution using the data of $Y_2Ni_3Si_5$ (Fig. 1), $\rho(T)$ of $Ce_2Ni_3Si_5$ in the high-temperature region is seen to have a negative slope with a broad maximum centered around 150 K and falls relatively sharply below 100 K. Such a behavior is typical of a valence-fluctuating system. For example, a similar $\rho(T)$ behavior has been observed in $CePd_3$.[10,11] Major features of valence-fluctuation phenomenon have been understood in terms of single-ion Kondo behavior and the resistivity drop at low temperatures has been ascribed to the onset of coherence.[12]

The resistivity at 300 K is rather high (300 $\mu\Omega$ cm) compared to that usually observed in metallic systems. ($\approx 40 \mu\Omega$ cm for $Y_2Ni_3Si_5$). It should be pointed out that it is even larger by a factor of 2–3 compared to that encountered ime ı sorof the Ce-based mixed-valence systems (e.g., 140 ℓ cr μʃn in CeRhIn,[13] and $CeIr_2Si_2$,[14] $\approx 110 \mu\Omega$ cn Ce in Pd$_3$.[11] Qualitatively, the overall temperature dependence of $\rho(T)$ of $Ce_2Ni_3Si_5$ is very similar to the above three compounds.

It may be remarked here that in $CePd_3$ a small shoulder was observed in the resistivity plot near 30 K and the pressure-dependent resistivity exhibits anomalies around 40 K. Lawrence *et al.*[15,16] have discussed this region in terms of temperature scale which correlates with the scale for the neutron scattering form factor anomaly and that this region might include growth of contributions from $5d$ electrons to the $4f$ form factor.[16,17] In the case of $Ce_2Ni_3Si_5$ we do not see such a shoulder, however a slight inflection is perceptible around 40 K.

In Ce-based valence-fluctuating systems, low-temperature behavior of resistivity has been found to vary as T^2 as expected of a Fermi liquid.[18] We find that our data fits well to a T^2 behavior over the temperature range 4.2–13 K (inset Fig. 1). A fit to $\rho = \rho_0 + AT^2$ yielded the values $\rho_0 = 53.9 \mu\Omega\,\mathrm{cm}$ and $A = 0.126 \mu\Omega\,\mathrm{cm\,K^{-2}}$. In the case of $CePd_3$, ρ_0 and A are reported to be 35.65 $\mu\Omega$ cm and 0.072 $\mu\Omega\,\mathrm{cm\,K^{-2}}$,[15] respectively. It is pertinent to point out here that in Eu-based valence-fluctuation compounds, $EuPd_2Si_2$, $EuNi_2P_2$, $EuIr_2Si_2$, $Eu_2Ni_3Si_5$, and $EuNiSi_2$, $\rho(T)$ at low temperatures varies as T^3.[19]

Figure 2 shows the magnetic susceptibility of $Ce_2Ni_3Si_5$ as a function of temperature in the range 5–300 K. In the high-temperature region (between 210 and 300 K), the susceptibility follows near Curie-Weiss behavior. A fit to Curie-Weiss formula gives $\mu_{\mathrm{eff}} \approx 2.55 \mu_B/\mathrm{Ce}$ ion with the paramagnetic Curie temperature $\theta_p \approx -190$ K. Although the value of μ_{eff} is similar to that of a free Ce^{3+} ion, a large value of θ_p is indicative of valence fluctuation in the compound. Quite often in materials of ternary rare-earth nickel systems, nickel ion does not carry a magnetic moment.[20] In our case we find that $Y_2Ni_3Si_5$ is not a Pauli paramagnet but very weakly magnetic with a Curie-Weiss behavior over the temperature range 4.2–300 K. The magnetic moment of the material is found to be $0.27 \mu_B$ per formula unit. If we attribute this moment as arising from Ni ions, it is indicative of a very small moment on Ni ($\approx 0.16 \mu_B$) in this material. Assuming that a similar situation as found above exists in $Ce_2Ni_3Si_5$ the μ_{eff}/Ce ion would be marginally lowered. Alternatively, this weakly magnetic response could be due to an impurity phase (< 5%, as the powder x-ray pattern does not in-

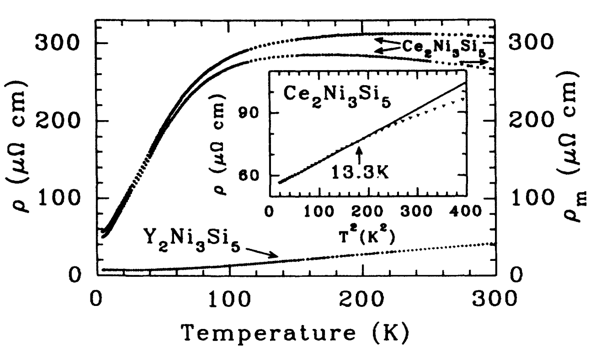

FIG. 1. Resistivity (ρ) of $Ce_2Ni_3Si_5$ as a function of temperature. ρ_m is the magnetic contribution to resistivity after subtracting the resistivity of $Y_2Ni_3Si_5$. The inset shows the T^2 behavior of resistivity in $Ce_2Ni_3Si_5$.

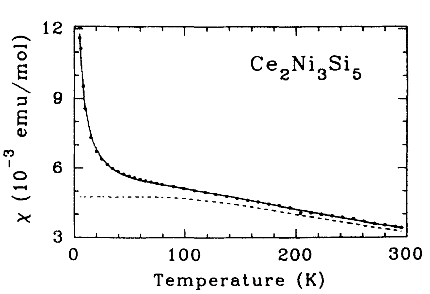

FIG. 2. Magnetic susceptibility of $Ce_2Ni_3Si_5$ as a function of temperature. The solid line shows a fit to the experimental data using Eq. (1) (see text). The dashed line is the susceptibility obtained from the fit after subtracting the impurity component (see text).

dicate any foreign phase) or due to some small magnetic impurity in the starting material. The magnetic susceptibility almost flattens out around 75 K but increases rapidly at lower temperatures ($T < 10$ K) which may be due to the presence of a small amount of nonfluctuating Ce^{3+} ions stabilized by lattice defects or traces of other magnetic impurity phases. However, as Gschneider argued[21] in the case of $CeSn_3$, such a feature ("Curie tail") may also be an intrinsic behavior arising out of an induced moment from 5*d* orbitals.

Often in Ce- and Yb-based valence-fluctuating compounds[22,23] χ shows a broad maximum and is due to the competition between the increased susceptibility with the decreasing temperature and the decrease due to decreasing population of the magnetic ions due to mixed valency. The existence of a maximum in the susceptibility of Ce- and Yb-based mixed-valence systems can be understood on the basis of an ionic two-level interconfiguration fluctuation model (ICF), of Hirst[24] and as also discussed by Sales and Wohlleben.[25] According to ICF model, the temperature dependence of the susceptibility (as modified by Franze *et al.*[26]) can be expressed as

$$\chi(T)=\left[\frac{N}{3k_B}\right]\left[\frac{\mu_n^2 v(T)+\mu_{n-1}^2[1-v(T)]}{\sqrt{T^2+T_{\rm sf}^2}}\right]$$

with

$$v(T)=\frac{(2J_n+1)}{(2J_n+1)+(2J_{n-1}+1)\exp\left[\dfrac{-E_{\rm ex}}{K_\beta\sqrt{(T^2+T_{\rm sf}^2)}}\right]}\,,$$

where $v(T)$ is the fractional occupation of ground-state configuration. Here $T_{\rm sf}$ is the spin fluctuation temperature (which we associated with the width of the energy level arising out of the fluctuation) which accounts for the fact that in mixed-valence systems the susceptibility at low temperatures is temperature independent. J_n, J_{n-1} and μ_n and μ_{n-1} are the total angular moment and effective paramagnetic moments of the states E_n and E_{n-1}, respectively. $E_{\rm ex}$ is the excitation energy between the ground state and the first excited state. At high temperature ($T \gg T_{\rm sf}$), this equation predicts a Curie-Weiss behavior of susceptibility but with an effective magnetic moment which is the populated weighted average of the moments of the individual states. The observed low-temperature tail, we believe, is due to the presence of some stable Ce^{3+} ions arising from a small amount of impurity. In order to apply an appropriate correction and to extract the intrinsic $\chi_{\rm int}(T)$ due to the Ce ions belonging to the material $Ce_2Ni_3Si_5$, we have added the term, $\chi_{\rm imp}=[nc/(T-\theta)]+\chi_0$, where n is the fraction of stable Ce^{3+} ions with a paramagnetic Curie temperature θ, and a Curie constant of c, and χ_0, a temperature independent term. Thus we get the relation

$$\chi(T)=(1-n)\left[\frac{N}{3k_B}\right]\left[\frac{\mu_n^2 v(T)+\mu_{n-1}^2[1-v(T)]}{\sqrt{T^2+T_{\rm sf}^2}}\right]+n\frac{c}{T-\theta}+\chi_0\,. \quad (1)$$

We have taken Ce^{4+} as the ground state and Ce^{3+} as the excited state and accordingly taken the magnetic moments of ground state and excited state as $0\mu_B$ and $2.54\mu_B$, respectively. A typical fit to the thermal susceptibility data using the above equation is shown in Fig. 2 as the solid line. The values of the parameters obtained by the least squares fitting are $E_{\rm ex}=285$ K, $T_{\rm sf}=140$ K, $n=0.027$, $\theta=-1.36$ K, $\chi_0=1.9\times10^{-4}$ emu/mol. The values of $E_{\rm ex}$ and $T_{\rm sf}$ are very typical as those observed in other Ce-based VF systems.[13]

Figure 3 gives the plot of heat capacity as a function of temperature in the form C/T vs T^2. The data exhibits a linear relationship over the temperature interval 2–20 K. A least-squares fit yielded a value of ≈ 62 mJ/Ce mol K^2 for the coefficient of the linear term in the heat capacity, γ. This value is considerably larger than that encountered in normal materials (≈ 10 mJ/Ce mol K^2) but is similar to those encountered in mixed-valence systems. The specific heat data do not show any anomaly in the temperature range where the "Curie tail" " is observed in the magnetic susceptibility and show conclusively that the system does not order magnetically at least down to 2 K.

Kadowski and Woods[27] have compiled the values of A and γ for a large number of heavy fermion and valence-fluctuation systems and have shown that there is a universal relationship between the resistivity and specific heat in these materials. This relationship is expressed in terms of the ratio A/γ^2 which is found to have a value of $\approx 1.0\times10^{-5}\mu\Omega$ cm (mol K^2/mJ)^2 for all the cases they considered.[27] $Ce_2Ni_3Si_5$ also seems to follow this relationship. In our case, (taking γ as 125 mJ/mol) $A/\gamma^2=0.8\times10^{-5}\mu\Omega$ cm (mol K^2/mJ)^2 which is not very different from that noted by Kadowasky and Woods.

There is another interesting relationship between the susceptibility, $\chi(0)$, at zero temperature and the low-temperature specific heat, γ, first derived by Lustfeld and Bringer[28] for the case of fully degenerate rare-earth impurity and later derived independently by Newns and

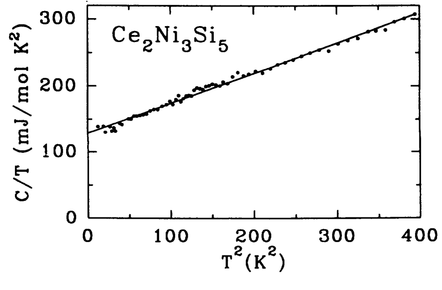

FIG. 3. Specific heat of $Ce_2Ni_3Si_5$ between 2–20 K. The solid line is a fit to the equation $C=\gamma T+\beta T^3$.

Hewson[29] on the basis of Fermi-liquid model for valence-fluctuating systems, viz.,

$$\frac{\chi(0)}{\gamma}=\frac{g^2\mu_B^2 J(J+1)}{\pi^2 k_B^2} .$$

Therefore, the so-called "Wilson ratio"

$$R=\frac{\pi^2 k_B^2 \chi(0)}{g^2\mu_B^2 J(J+1)\gamma}$$

should be unity. We find that in $Ce_2Ni_3Si_5$, with the ICF model extrapolated $\chi(0)$ of 4.74×10^{-3} emu/mol, and γ of 125 mJ mol^{-1} K^{-2}, R comes out to be ≈ 1.30. In the case of $CePd_3$ $\chi(0)\approx 1.47\times10^{-3}$ emu/mol,[29] and $\gamma \approx 37$ mJ mol^{-1} K^{-2},[30] and $CeSn_3$ $\chi(0)\approx 1.46\times10^{-3}$ emu/mol,[31] and $\gamma\approx 53$ mJ $mol^{-1} K^{-2}$,[32] R was found to be 1.36 and 0.96, respectively.[29]

In conclusion, we have shown through resistivity, magnetic susceptibility, and specific heat measurements that Ce is in the mixed-valence state in the compound $Ce_2Ni_3Si_5$. The low-temperature resistivity behavior is shown to be $\rho(T)\approx\rho(0)+AT^2$ as observed in many other Ce-based mixed-valence systems. These features are consistent with the Fermi-liquid-like nature of the system at low temperatures.

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