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Superconductivity in the ternary nickel silicide $Lu_2Ni_3Si_5$

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The synthesis and results of electrical-resistivity (1.5–300 K), ac-magnetic-susceptibility (1.5–5 K), and specific-heat (1.7–30 K) measurements are reported on a ternary rare-earth–nickel-silicide compound $Lu_2Ni_3Si_5$. The compound is found to be superconducting below 2.1 K. The magnetic-susceptibility measurements show the onset of diamagnetism at 2.1 K and the resistivity goes to zero at 2.0 K with the same onset temperature. The resistivity above the transition temperature shows a metallic behavior. A deviation from linear resistivity at high temperatures implies a short mean free path. The heat capacity shows a jump with a peak at 1.9 K, which indicates bulk superconducting ordering in this sample. The estimated value for $\gamma(=C_p/T$ as $T\rightarrow 0)$ is 5.8 mJ/Lu mol K^2 and $\Delta C_p/\gamma T_c$ is 1.1, which is lower than the BCS value of 1.43. From these results, we conclude that $Lu_2Ni_3Si_5$ is a weak-coupling BCS superconductor.

I. INTRODUCTION

After the discovery of high temperature superconductivity in ceramic systems,[1] interest in the conventional intermetallic superconductors has somewhat declined. Intermetallic superconductors are still of relevance. In the area of applications, intermetallic superconductors have an advantage over ceramic superconductors as they are much less brittle compared to ceramics and therefore can be drawn in the form of wires. Recently we discovered superconductivity in Ni-containing quaternary Y-Ni-B-C systems at an elevated temperature ($T_c \approx 12$ K).[2–4] Replacing Ni by Pd has led to the multiphase Y-Pd-B-C system, which has a large T_c for bulk intermetallics [$T_c \approx 23$ K,[5] $T_c \approx 22$ K (Ref. 6)]. Interest in intermetallic superconductors has been revived because of these studies. Although these materials do not have as high a T_c as ceramic superconductors, their T_c's are comparable to those of other oxide materials, such as $BaPb_{1-x}Bi_xO_3$ ($T_c \approx 13$ K)[7] or even the Ba-La-Cu-O ($T_c \approx 30$ K) system.[1] As a consequence of these results, there are expectations of new intermetallic superconductors with higher T_c's. Continuing with our search of Ni-containing superconductors, we observed superconductivity at about 2 K in the material $Lu_2Ni_3Si_5$. In this paper we present our results on the measurements of the superconducting properties of this material.

In the past, a lot of attention had been given to ternary superconductors, particularly to the series $R_2Fe_3Si_5$, because of their relatively high T_c's even though magnetic element Fe constitutes 30 at. % of the composition of the material.[8] It has been shown by Mössbauer measurements that the Fe ions do not carry any magnetic moment in this structure.[9] Superconductivity is suppressed if Fe is replaced by one of the isoelectronic elements Ru or Os.[10] Partial substitution of Fe by magnetic ions such as Cr or Ni, are also known to suppress superconductivity but at a much faster rate.[11] For instance, 1 at. % of Cr in $Lu_2Fe_3Si_5$ brings the value of T_c down from 6 K to ~2 K, and 2 at. % Ni produces a similar effect.

When Fe is completely replaced by Ni in $R_2Fe_3Si_5$ (R =Y, Ce, Dy), the structure changes from tetragonal (space group $P4/mnc$) to orthorhombic $U_2Co_3Si_5$ structure (space group $Ibam$).[12] In our continuing studies of the physical properties of the series $R_2Ni_3Si_5$ (R = rare earth, Y), we showed that R-ions in $Ce_2Ni_3Si_5$ and in $Eu_2Ni_3Si_5$ are in a valence-fluctuating state.[13,14] The other members of the series $R_2Ni_3Si_5$ (R = Ce−Nd, Sm−Ho) also form in the orthorhombic $U_2Co_3Si_5$ structure. All of them, except for $Ce_2Ni_3Si_5$ and $Eu_2Ni_3Si_5$, order magnetically.[15–17] However, a change in structural pattern has been observed in $R_2Ni_3Si_5$ beyond R = Ho.[18] These materials tend to form in a monoclinic structure. In this paper, we report the synthesis of $Lu_2Ni_3Si_5$. ac-susceptibility, resistivity, and heat-capacity results show that $Lu_2Ni_3Si_5$ undergoes bulk superconducting ordering below 2 K.

II. EXPERIMENTAL

The compound $Lu_2Ni_3Si_5$ was synthesized by melting together stoichiometric amounts of constituent elements of high purity (Lu ≥99.9%, Ni ≥99.9%, Si ≥99.999%) in an arc furnace (Centor, USA) under a flowing argon atmosphere. The ingots were melted six times, flipping after each melting to ensure homogeneity. The loss in weight in this process was negligible (≤0.1%). Subsequently, each sample was wrapped in a tantalum foil and sealed in a quartz tube in vacuum and put for annealing at 1100 °C for eight days, after which it was slowly cooled to room temperature. Two independent batches of materials, with starting materials obtained from different sources, were synthesized. The x-ray-powder-diffraction (XRD) patterns of the polycrystalline samples

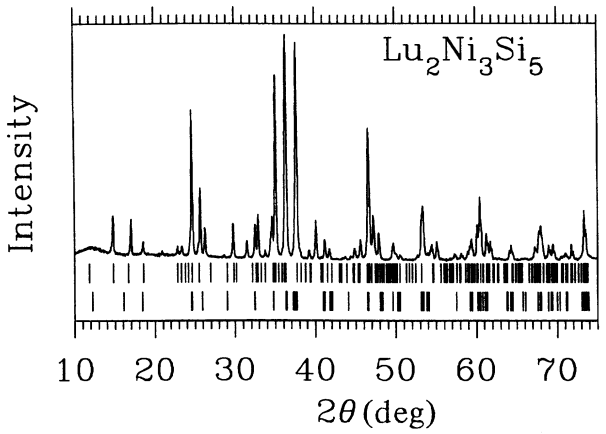

FIG. 1. Room-temperature powder-x-ray-diffraction pattern of $Lu_2Ni_3Si_5$. The upper bars correspond to the positions of XRD peaks permitted by the space group *C2/c*, while the lower bars correspond the positions permitted by space group *Ibam*.

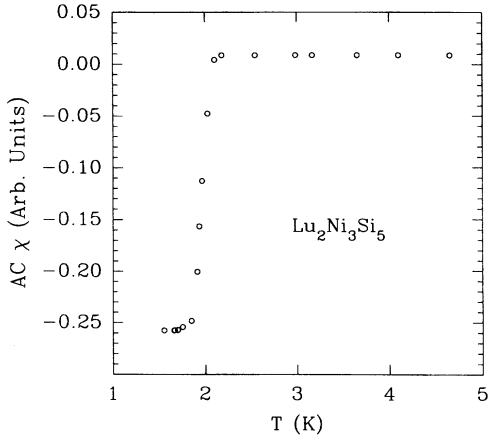

FIG. 2. ac susceptibility of $Lu_2Ni_3Si_5$ from 1.5 to 5 K.

were studied at room temperature on a commercial diffractometer (Jeol, Japan) using Cu $K\alpha$ radiation. The ac-susceptibility was measured from 1.5 to 5 K using a home built susceptometer.[19] The resistivity was measured from 1.5 to 300 K, using a four-probe dc technique. The contacts for the electrical leads were made ultrasonically (with non-superconducting solder) on a rectangular sample of the size 2.5 mm×3 mm×0.8 mm. The heat capacity in zero field was measured between 1.7 and 30 K using an automated adiabatic heat calorimeter in which a calibrated germanium resistance (Lake Shore Inc., USA) was used as the temperature sensor.

III. RESULTS AND DISCUSSION

The room temperature powder-x-ray-diffraction (XRD) pattern of $Lu_2Ni_3Si_5$ (Fig. 1) shows a few extra lines that could not be indexed in terms of the $U_2Co_3Si_5$-type structure (space group *Ibam*); the pattern looks very much similar to that of other members of the series $R_2Ni_3Si_5$ (R = Ce–Nd, Sm–Ho). An effort to fit (by the Rietveld refinement procedure) the XRD pattern with the $U_2Co_3Si_5$-type structure led to the following lattice parameters: a = 9.604 Å, b = 11.014 Å, and c = 5.512 Å. Here it should be pointed out that in most of the cases, where lighter members of a rare-earth series of compounds form in the $U_2Co_3Si_5$-type structure, compounds with heavy rare-earth elements form in the monoclinic variation of the $U_2Co_3Si_5$-type structure—commonly referred to as the $Lu_2Co_3Si_5$-type structure (space group *C2/c*).[20] Rietveld refinement of the XRD data of $Lu_2Ni_3Si_5$ (assuming atomic positions to be the same as those in the case of $Lu_2Co_3Si_5$) though gave a better fit and accounted for more lines (except a few small lines of intensity $\leq$15%), there being considerable difference in the intensities. The fit resulted in the following values of cell parameters: a = 11.032 Å, b = 11.942 Å, and c = 5.919 Å, β= 120.18°. Both the batches of materials showed very similar results. A single-crystal study is required to resolve the structure properly. The energy dispersive x-ray analysis (EDAX) showed the homogeneous nature of the material with an elemental ratio which is very close to the expected composition.

The ac magnetic susceptibility of $Lu_2Ni_3Si_5$ in the temperature range 1.5 to 5.0 K (Fig. 2) shows a diamagnetic behavior below 2.1 K. This behavior has been confirmed on the sample from the second batch also. The dc resistance of the material shows a drop at T_c(onset) = 2.1 K and goes to zero at 2.0 K. Both of these measurements establish the superconducting state below 2.1 K (Fig. 3). Above the superconducting transition, the material shows a metallic behavior. However, unlike $Y_2Ni_3Si_5$, where the resistivity behavior is almost linear in the high-temperature range,[13] the resistivity data of $Lu_2Ni_3Si_5$ show a deviation from linear temperature dependence, which is possibly because of a smaller mean free path. It is understandable, as Lu ions have a smaller size than Y ions. Such a deviation from linear temperature dependence has been seen in many alloys, in which cases a saturation is also observed at high temperature. The saturation is attributed to the high value of ρ of these alloys at high temperatures. This behavior has also been seen in previous studies on silicides.[21]

One of the models that describes the deviation of $\rho(T)$

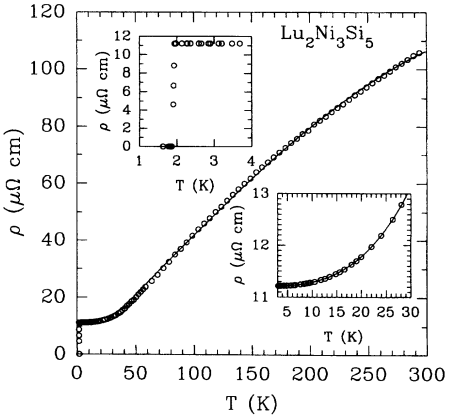

FIG. 3. Resistivity of $Lu_2Ni_3Si_5$ from 1.5 to 300 K. The solid line is a fit to Eq. (2). The insets show the superconducting transition and a T^3 dependence of $\rho(T)$ at low temperatures. Solid lines are fit to the models (see text).

from linear behavior at high temperatures ($50<T<300$ K in our case) in a nonmagnetic material, is the parallel resistor model.[22] In this model, the expression of $\rho(T)$ is given by

$$\frac{1}{\rho(T)}=\frac{1}{\rho_1(T)}+\frac{1}{\rho_{\max}}, \tag{1}$$

where $\rho_{\max}$ is the saturation resistivity that is independent of temperature and $\rho_1(T)$ is the ideal temperature-dependent resistivity. The ideal resistivity is given by the following expression:

$$\rho_1(T)=\rho_0+C_1\left(\frac{T}{\Theta_D}\right)^n\int_0^{\Theta_D/T}\frac{x^n dx}{[1-\exp(-x)][\exp(x)-1]}, \tag{2}$$

where $\rho(0)$ is the residual resistivity. The second term is due to phonon-assisted electron scattering similar to the s-d scattering in transition-metal alloys where $x=\hbar\nu/kT$ and ν is the phonon frequency. The value of n is 3 for the Wilson model of s-d scattering[23,24] and is 5 for the Bloch-Grüeniesen model.[23,24] Θ_D is the Debye temperature and C_1 is a numerical constant. The resistivity data were fit to the above equations in the range 50–300 K. We get a better fit with $n=3$. It may be noted that both the models give a linear temperature dependence at high temperatures. The fit yielded $\rho_0=12$ $\mu\Omega$ cm and $\Theta_D=365$ K, which is close to the value measured by the heat-capacity study (see below). The resistivity data at low temperatures ($3<T<30$ K) were fit to the expression

$$\rho(T)=\rho_0+AT^m,$$

where ρ_0 is the residual resistivity and A is a constant. We get a good fit for $m=3$. Thus, the low-temperature resistivity shows a T^3 dependence, as expected from the s-d scattering model.[23,24]

The heat capacity of $Lu_2Ni_3Si_5$, shows a jump with a peak at 1.9 K confirming the bulk nature of superconductivity (Fig. 4). The temperature coefficient of the electronic heat capacity, γ, was obtained from the extrapolation of heat-capacity data in the temperature range 3–30 K to $T=0$ K. The specific-heat data have been fit to the equation

$$C_p/T=\gamma+\beta T^2+\delta T^4. \tag{3}$$

A fit to this equation gives a value of $\gamma=5.8$ mJ/mol K^2, $\beta=0.42$ mJ/mol K^4, and $\delta=6.7\times10^{-4}$ mJ/mol K^6. The anharmonic term δ was observed in the $R_2Fe_3Si_5$ system also.[25] Using the relation

$$\Theta_D=\left(\frac{1944\times10^3 N}{\beta}\right)^{1/3} \tag{4}$$

(where N is the number of atoms per formula unit, β is in mJ/mol K^4, and Θ_D is in kelvin) Θ_D was obtained as 359 K.

In order to get further insight into the superconducting behavior of $Lu_2Ni_3Si_5$, we calculated $\Delta C/\gamma T$ at $T=T_c$ and found it to be 1.1. This value is sufficiently close to ($\approx80\%$) but less than the BCS value of 1.43 for this term. Such a reduced value of the heat-capacity jump has been reported in $R_2Fe_3Si_5$ systems also.[25] Based on these considerations, we conclude that $Lu_2Ni_3Si_5$ is a weak-coupling BCS superconductor.

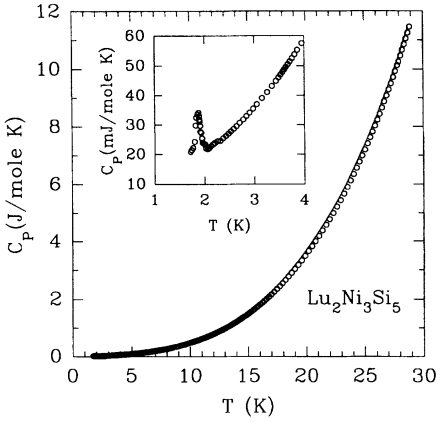

FIG. 4. Temperature dependence of specific heat of $Lu_2Ni_3Si_5$ from 1.7 to 30 K. The inset shows an expanded plot at low temperatures. The solid line is a fit to Eq. (3).

It is not clear to us if Ni atoms in $Lu_2Ni_3Si_5$ carry any moment as we have not performed any dc magnetic measurements on $Lu_2Ni_3Si_5$. Our dc magnetic susceptibility of $Y_2Ni_3Si_5$ could be fit with an effective moment of $0.27\mu_B$/formula unit, which is equivalent to $0.16\mu_B$/Ni ion.[13] However, in the orthorhombic $U_2Co_3Si_5$-type structure, there are two nonequivalent Ni sites and there is a possibility of two Ni sites having different moments. The same is true in the monoclinic $Lu_2Co_3Si_5$-type structure also. dc magnetic measurements and other spectroscopic techniques are required to resolve this issue in $Lu_2Ni_3Si_5$.

IV. CONCLUSIONS

In conclusion, we have shown that the material $Lu_2Ni_3Si_5$ is a bulk superconductor with $T_c\approx2$ K. There are only three nickel-based ternary superconductors known, Ni_2NbAl ($T_c=2.15$ K), Ni_2NbGa ($T_c=1.54$ K), and Ni_2NbSn ($T_c=2.90$ K).[26] $Lu_2Ni_3Si_5$ is a nickel-based superconducting ternary rare-earth compound. In $Lu_2Fe_3Si_5$ (tetragonal structure), Fe atoms do not carry any magnetic moment, i.e, the Fe d band is completely filled. It is known that small amounts of Ni suppress T_c in $Lu_2Fe_3Si_5$.[11] However, in structurally different $Lu_2Ni_3Si_5$, one observes superconductivity which suggests that the crystal structure plays a role in sustaining superconductivity in this compound. In this context it will be of interest to study the effect of Fe in $Lu_2Ni_3Si_5$. Such studies are in progress. Finally, it is important to know if Ni atoms in $Lu_2Ni_3Si_5$ have a moment. This needs further study.

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