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Crystal structure and superconductivity in the Ni-based ternary compound LaNiSi

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With powder-x-ray-diffraction methods, the ternary compound LaNiSi has been identified to have a LaPtSi-type crystal structure with four formula units in a unit cell of the space group $I4_1md$ with dimensions $a=4.181(1)$ Å, $c=14.069(8)$ Å. The agreement of the transition temperature $T_c=1.20\sim1.26$ K (10~90 % values) measured by ac-susceptibility and heat-capacity techniques provides clear evidence of bulk superconductivity in LaNiSi. The normal-state specific-heat data can be fit to the expression $C_n=\gamma T+\beta T^3$ by a least-squares analysis, where $\gamma=8.89$ mJ/mol K^2 and $\beta=0.487$ mJ/mol K^4, resulting in a Debye temperature $\Theta_D=229$ K. Below T_c, the specific-heat data have a dominant low-temperature behavior of the form $\exp[-\Delta(0)/k_BT]$, where the order parameter $2\Delta(0)=3.5k_BT_c$. In addition, the measured heat-capacity jump ΔC at the transition point is found to be equal to $1.46\gamma T_c$, implying that LaNiSi is a weakly coupled superconductor.

Recently there have been some notable discussions on the existence of superconductivity in nickel-based ternary or quaternary intermetallic compounds.[1-4] As mentioned by Nagarajan *et al.*,[2] only a small number of nickel-containing binary superconductors are known in the literature and no Ni-based ternary superconductor was previously reported until the discovery of the superconductivity in Y-Ni-B. Clearly, the ferromagnetic element Ni in a compound usually has an adverse effect on the superconductivity properties. Thus, the identification of superconducting Ni-based compounds is of high current interest. In this paper, we report superconductivity in the compound LaNiSi. To our knowledge, this is the first nickel-based ternary-silicide superconductor. As shown by ac-susceptibility and heat-capacity measurements, this compound undergoes a superconducting transition at 1.23 K (the midpoint of the transition). We have also determined the crystal structure and lattice parameters of a unit cell for this compound using powder-x-ray-diffraction analysis.

Polycrystalline LaNiSi was synthesized by arc melting stoichiometric amounts of the constituent elements in a Zr-gettered arc furnace on a water-cooled Cu hearth under purified argon of about 1 atm. La with a purity of 99.9% was obtained from the Materials Preparation Center of the Ames Laboratory. Ni with 99.9% purity and Si with 99.999 999 9% purity were purchased from Morton Thiokol, Inc. and Matthey Bishop, Inc., respectively. Due to sufficiently low vapor pressures of these elements at the melting temperature of the ternary compound, weight losses during several melting and turning cycles were less than 0.1%. The arc-melted sample was then wrapped in tantalum foil and zirconium foil, sealed under argon in a quartz tube, and annealed for 10 days at 1000 °C. This heat treatment was followed by a water quench to room temperature. A microcomputer-controlled MXP3 diffractometer equipped with a copper target and a graphite monochromator for $K\alpha$ radiation was used to obtain the powder-x-ray-diffraction (XRD) patterns. As shown in Fig. 1, each peak line of the XRD pattern for LaNiSi can be indexed in a tetragonal LaPtSi-type structure[5] with space group $I4_1md$. In fact, no traces of secondary phases were observed at higher angles. A refinement of the lattice parameters of the unit cell was determined by the method of least squares using the eight intense reflections for $2\theta<50°$ and by including an internal silicon standard ($a=0.543\ 083$ nm). The lattice parameters $a=4.181(1)$ Å, $c=14.069(8)$ Å were then obtained. A comparison of the calculated line intensities with those determined experimentally showed reasonable agreement. In this comparison, we employed the standard atomic positional parameters for the atoms in the unit cell. Specifically, the atoms were all placed in the $4a$ position of the space group $I4_1md$ (the 109th space-group number) with fractional coordinates: La(0,0,0), Ni(0,0,0.585), and Si(0.0,0.419). The agreement of intensities indicates that no significant antisite disorder or vacancies are present in our sample. Four formula units of LaNiSi constitute the unit cell.

The low-temperature ac-magnetic-susceptibility measure-

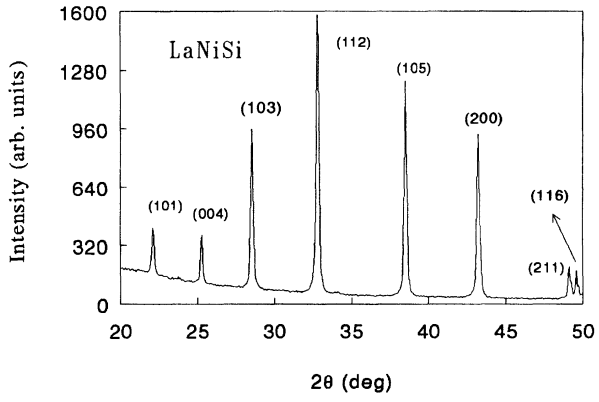

FIG. 1. Room-temperature powder-x-ray-diffraction pattern of LaNiSi using Cu $K\alpha$ radiation.

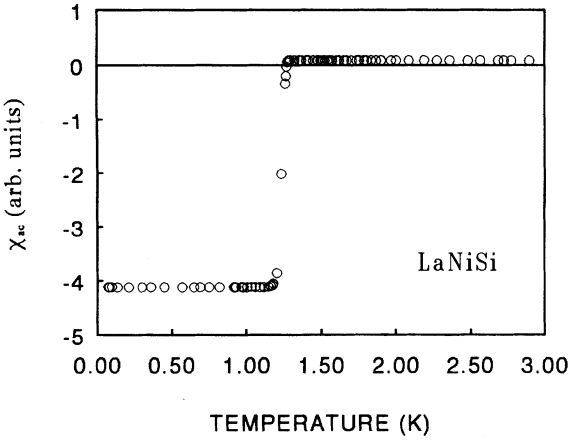

FIG. 2. χ_{ac} vs T of LaNiSi between 70 mK and 3.0 K.

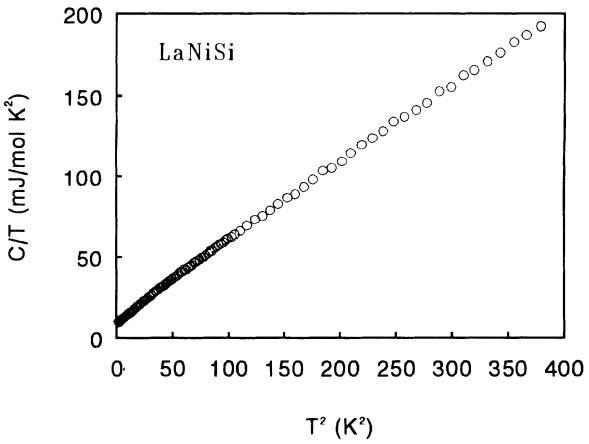

FIG. 4. Specific heat divided by temperature C/T vs T^2 of LaNiSi between 1.3 and 20 K. The value of γ was obtained by extrapolating the specific heat in this plot of C/T vs T^2 down to 0 K.

ments were performed in a He^3-He^4 dilution refrigerator down to 70 mK.[6] A lock-in amplifier served to measure these signals and a germanium thermometer calibrated to an accuracy within 0.1% was used to determine the temperatures. Figure 2 presents the temperature dependence of the ac magnetic susceptibility χ_{ac} for the compound LaNiSi measured in a temperature range 70 mK–3 K. It is seen that the 10–90% values of the superconducting transition signal occur at the temperatures 1.20 and 1.26 K. The quite narrow transition width (0.06 K) is a manifestation of high purity of the sample phase. The strong diamagnetic signal of χ_{ac} alone does not prove the existence of bulk superconductivity in LaNiSi. Convincing evidence for superconductivity is a specific-heat anomaly.

The specific heat of a piece (~3 mg) cut from the sample was measured in the range of 0.7–20 K with a He^3 relaxation calorimeter using the heat-pulse technique[7] in the earth's magnetic field. The sample was attached to a sapphire chip, which has two separated silicon films deposited on it to serve as heater and thermometer. The calibration of the thermometer was done against a calibrated germanium thermometer. For each point of the specific-heat measurements, a small heat power was introduced to the chip and the thermal relaxation was measured and analyzed to obtain the specific heat of the sample. Figure 3 displays the temperature dependence of the specific C for the compound LaNiSi between 0.7 and 3 K. In both χ_{ac} and C measurements the transition occurs over an interval of about 0.06 K (10–90% values). The agreement of the transition temperatures measured by both techniques is clear evidence of bulk superconductivity in LaNiSi. The specific-heat data plotted as C/T against T^2 in Fig. 4 show that the heat capacity C of LaNiSi, in the normal state at temperatures below 20 K, can be fit to the expression $C_n=\gamma T+\beta T^3$ by a least squares analysis, which yields the value $\gamma=8.89$ mJ/mol K^2 and $\beta=0.487$ mJ/mol K^4, the latter value corresponding to the Debye temperature $\Theta_D=289$ K. For comparison to γ, we have estimated γ_{BCS} from the measured specific-heat jump ΔC (16 mJ/mol K) at T_c (1.23 K) using the Bardeen-Cooper-Schrieffer (BCS) relation, $\gamma_{BCS}=\Delta C/1.43T_c\sim 9.09$ mJ/mol K^2. The observed value

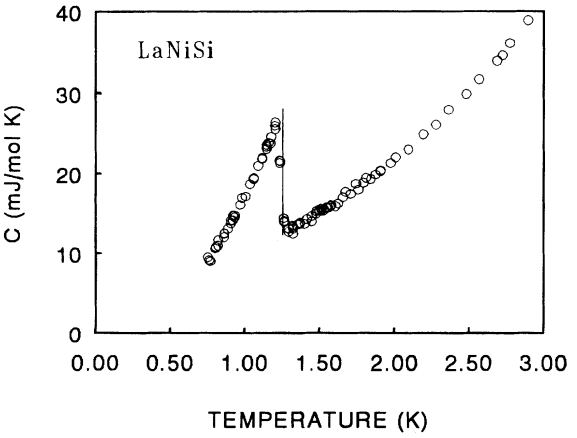

FIG. 3. Heat capacity of LaNiSi between 0.7 and 3 K in the earth's field.

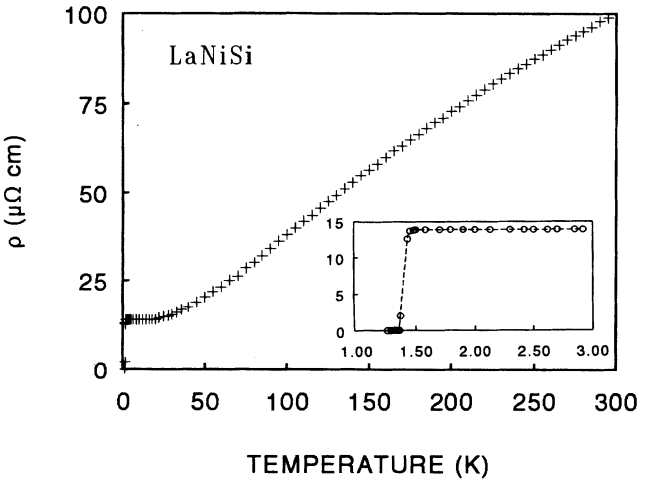

FIG. 5. Electrical resistivity vs temperature between 1.26 and 300 K for LaNiSi. Inset: ρ vs T between 1.26 and 3.0 K.

of γ (8.89 mJ/mol K^2) is in good agreement. According to the microscopic theory of superconductivity, the specific-heat data below T_c have a dominant low-temperature behavior of the form $\exp[-\Delta(0)/k_BT_c]$. Analysis of our data shown in Fig. 3 provides evidence for the gap to be of the order of 3.6 meV, that is, $2\Delta(0) = 3.5k_BT_c$ as predicted by the weak-coupling BCS model.

Dc electrical resistivity measurements were made between 2.0 and 300 K using a standard four-probe technique in a Quantum Design system fully automated for temperature stability and data acquisition.[8] However, because of the low transition temperature of the sample, the ac electrical resistivity data between 1.26 and 3 K were also measured using a standard four-probe phase-sensitive detection technique at a low frequency of ~25 Hz in a He^4 dewar. Fine platinum wires (~2 mil diam) were spot-welded to the rectangular-shaped sample and served as the voltage and current leads. The complete resistivity data between 1.26 and 300 K for the polycrystalline sample LaNiSi are presented in Fig. 5. It is seen that the residual resistivity and residual resistivity ratio values for superconducting LaNiSi are 13.9 $\mu\Omega$ cm and 7.2, respectively. The zero resistance temperature (1.36 K) shown in the inset of Fig. 5 is slightly higher than the transition point value obtained by ac-susceptibility and heat-capacity measurements. This phenomenon is probably due to the surface superconductivity[9,10] of this compound.

As a concluding remark, the Ni-based intermetallic compound LaNiSi, which crystallizes in the LaPtSi-type structure, exhibits phonon-mediated superconductivity with $T_c \sim 1.23$ K as characterized by the specific-heat, magnetic, and resistivity data.

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