Superconductivity at 15 K in the metastable $ScNi_2B_2C$ compound

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A superconducting transition around 15–16 K is reported for metastable, as-melted $ScNi_2B_2C$ samples. Zero resistivity T_c(zero) was observed at 14.6 K with T_c(onset) around 16.5 K. A consistent diamagnetic T_c signal was observed around 14.8–15.6 K. The new superconducting phase was identified as isostructural to the quaternary $LuNi_2B_2C$-type phase with tetragonal lattice parameters $a = 3.34$ Å and $c = 10.2$ Å. This superconducting phase is unstable due to the extremely small Sc^{3+} ionic size, where the Sc atom is located in the cavity formed by the B-Ni-B-C network and no superconducting transition could be observed down to 5 K after 1050 °C annealing.

Superconducting intermetallic compounds with relatively high transition temperatures up to 23 K have been reported in *R*-*T*-B-C systems, where *R* = Y or rare earths and *T* = Ni, Pd, or Pt.[1–5] In the nickel-based system, the superconducting phase has been identified as a quaternary $LuNi_2B_2C$-type tetragonal structure with space group *I4/mmm*. The structure is a three-dimensionally connected framework with LuC NaCl-type layers alternated with Ni_2B_2, layers where nickel is tetrahedrally coordinated by four boron atoms.[4] The phase formation was reported in RNi_2B_2C (*R* = Y, La, Ce, Sm, Tb, Dy, Ho, Er, Tm, or Lu) with a maximum T_c of 16.6 K for nonmagnetic $LuNi_2B_2C$, and a next-highest T_c of 15.6 K for nonmagnetic YNi_2B_2C.[1,3,4] For magnetic rare-earth compounds, a lower superconducting transition was observed for *R* = Ho, Er, and Tm, due to the magnetic pair-breaking effect.[3] Here we report the discovery of a high-T_c metastable compound $ScNi_2B_2C$, which is isostructural to $LuNi_2B_2C$.

All RNi_2B_2C (*R* = Sc or Lu) samples were prepared by arc melting the high-purity elements (Sc and Lu: 99.9%; Ni: 99.999%; B: 99.9995%; and C: 99.999%) under an argon atmosphere in a Zr-gettered arc furnace. A two-stage procedure (RNi_2B_2 + C) was utilized with negligible weight loss (less than 2%). Crystallographic data were obtained with a Rigaku Rotaflex rotating anode powder x-ray diffractometer using Cu $K\alpha$ radiation with a scanning rate of 1° in 2θ per minute. A Lazy Pulverix-PC program was employed for phase identification and lattice parameter calculation. Low-field magnetic measurements were made with either a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer (≥ 20 G) or a MPMS2 (≤ 20 G) SQUID magnetometer down to 5 K. ac electrical resistivity measurements (16 Hz) were carried out by the standard four-probe method in a RMC-Cryosystems closed-cycle refrigerator down to 7 K.

Powder x-ray diffraction data for all as-melted $ScNi_2B_2C$ samples show multiphase patterns. However, a pattern search indicates that the major phase can be indexed as the $LuNi_2B_2C$-type tetragonal structure (space group *I4/mmm*), with lattice parameters $a = 3.34(1)$ Å, $c = 10.2(1)$ Å and unit-cell volume $V = 114(1)$ Å^3. These values are smaller than $a = 3.464$ Å, $c = 10.63$ Å and $V = 127.6$ Å^3 for isostructural $LuNi_2B_2C$ due to the smaller Sc^{3+} ionic radius of 0.732 Å as compared with 0.85 Å for the larger Lu^{3+} ion.[4]

Two samples (*A* and *B*) with better x-ray diffraction patterns were used for transport and magnetic measurements. The temperature dependence of the electrical resistivity $\rho(T)$ for the as-melted $ScNi_2B_2C$ sample *A* is shown in Fig. 1. Zero resistivity T_c(zero) was observed at 14.6 K, with the superconducting onset (1%) T_c(onset)

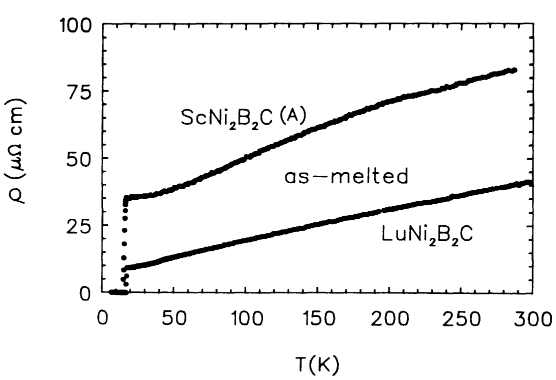

FIG. 1. Temperature dependence of electrical resistivity $\rho(T)$ for as-melted $ScNi_2B_2C$ (sample *A*). Data for stable, isostructural 16.6-K superconductor $LuNi_2B_2C$ are also included for reference.

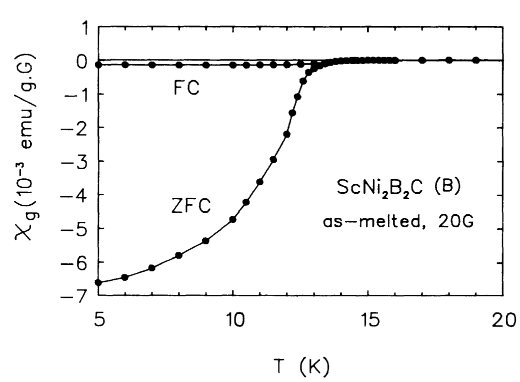

FIG. 2. Low-temperature mass magnetic susceptibility $\chi_g(T)$ for as-melted $ScNi_2B_2C$ (sample *B*).

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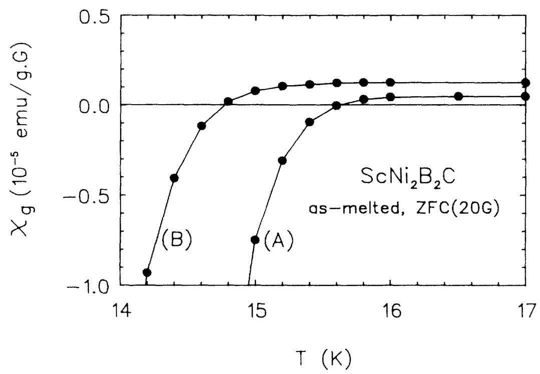

FIG. 3. Superconducting transition onset from diamagnetic measurements for as-melted $ScNi_2B_2C$ (samples A and B).

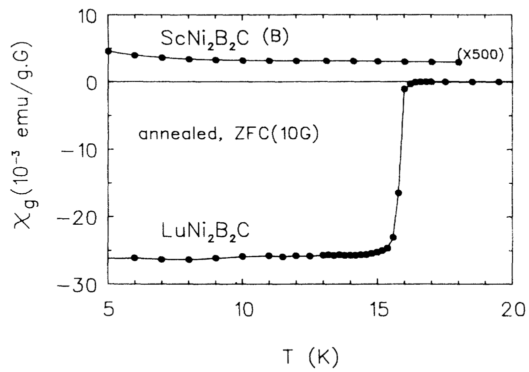

FIG. 4. Low-temperature mass magnetic susceptibility $\chi_g(T)$ for 1050°C annealed $ScNi_2B_2C$ (sample B) and $LuNi_2B_2C$.

around 16.5 K. The room-temperature resistivity is 82.8 $\mu\Omega$ cm, with a resistivity ratio $\rho(RT)/\rho(20\text{ K})$ of 2.33. Data for isostructural superconductor $LuNi_2B_2C$ are also included with T_c(zero) at 16.7 K and T_c(onset) around 17.6 K. The room-temperature resistivity is 41.2 $\mu\Omega$ cm, with a resistivity ratio $\rho(RT)/\rho(20\text{ K})$ of 4.43.

The low-temperature mass magnetic susceptibility $\chi_g(T)$ of the second as-melted $ScNi_2B_2C$ sample B is shown in Fig. 2 for both zero-field-cooled (ZFC) and field-cooled (FC) measurements in a low applied field of 20 G. A diamagnetic superconducting transition signal was observed around 14.8 K for this sample. A large ZFC shielding signal of -6.7×10^{-3} emu/(g G) at 5 K for the bulk sample indicates that the bulk superconductivity effect (using the calculated x-ray density of 5.42 g/cm^3). For the powdered sample (200 mesh), the diamagnetic shielding signal decreases to -1.7×10^{-3} emu/(g G) due to the multiphase nature of the as-melted sample.

The diamagnetic T_c transition is field independent in a low applied field of 5–50 G, but slightly sample dependent due to different arc-melting conditions. The highest diamagnetic T_c signal around 15.6 K for sample A was observed, as compared with 14.8 K for sample B (Fig. 3).

Contrary to the stable superconducting $LuNi_2B_2C$ phase, superconductivity in as-melted $ScNi_2B_2C$ samples is metastable. After annealing the samples at 1050°C in a sealed quartz tube (wrapped in Ta foil and then sealed under argon) for 24 h and water quenching, no superconducting transition can be observed down to 5 K from the low-temperature mass magnetic susceptibility $\chi_g(T)$ data (Fig. 4). The x-ray powder diffraction patterns for annealed samples show no trace of the tetragonal $LuNi_2B_2C$-type phase, indicating that this superconducting tetragonal phase is entropy stabilized during the arc-melting process. Contrary to the weak, temperature-dependent, Pauli-like paramagnetic behavior of the annealed $ScNi_2B_2C$ sample [$+9.1\times10^{-6}$ emu/(g G) at 5 K], the annealed $LuNi_2B_2C$ bulk samples exhibits an excellent T_c transition of 16.7 K with a large and almost temperature-independent ZFC shielding signal of -2.62×10^{-2} emu/(g G) (x-ray density 8.49 g/cm^3).

The entropy-stabilized or metastable tetragonal phase in $ScNi_2B_2C$ is apparently closely related to the size effect. Since the $LuNi_2B_2C$-type phase is a variant on the $ThCr_2Si_2$-type structure with additional carbon in the Lu plane, the Lu atom is located in the cavity formed by the B-Ni-B-C network.[4] After the substitution of small Lu ions by even smaller Sc, the structure is thus highly unstable and the phase exists only in the high-temperature, high-entropy region of the phase diagram, with an exceptionally small tetragonal c lattice parameter. Similar metastability due to the size effect was observed in many other superconducting systems. For example, in the RRu_4B_4 system, the metastable phase was observed for the 7.2-K $ScRu_4B_4$ superconductor, as compared with the stable 2.1-K $LuRu_4B_4$ superconductor.[6] In the superconducting RIr_4B_4 systems (R = Ho, Er, or Tm), all superconducting $ErRh_4B_4$-type phases are metastable.[7] The unstable 23-K Y-Pd-B-C phase[2] is probably due to a similar origin, where the high-T_c YPd_2B_2C-type phase can be stabilized only with the off-stoichiometric composition of $YPd_5B_3C_{1-x}$.

The T_c of 15–16 K for the present metastable $ScNi_2B_2C$ compound is only slightly lower than 16.7 K for the $LuNi_2B_2C$ compound, and almost equal to 15.6 K for the YNi_2B_2C compound (with a larger Y^{3+} ionic radius of 0.893 Å), which indicates that the superconducting properties in this system may be irrelevant to the relative size of nonmagnetic R^{3+} ions (R = Sc, Y, or Lu). Detailed studies of metastability, lattice parameter variation, and superconducting properties of the pseudoquaternary $(Lu_{1-x}Sc_x)Ni_2B_2C$ system are in progress. Preliminary results indicate that the unstable boundary is near the Sc-rich region ($x>0.5$), with a stable T_c of 15.9 K for the $(Lu_{0.5}Sc_{0.5})Ni_2B_2C$ compound. For the $LuNi_2B_2C$ compound ($x=1$), a lower critical filed H_{c1}(15 K) of 70 G and an upper critical field H_{c2}(15 K) of 7 kG were observed from magnetization $M(H)$ measurements for this type-II superconductor.

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