Metal-insulator transition of RNiSn (R=Zr, Hf, Ti) intermetallic vacancy systems

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(Submitted 15 April 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 11, 535–537 (10 June 1987)

Anomalous kinetic and optical properties have been detected in a new class of intermetallic compounds: RNiSn (R = Zr, Hf, Ti), characterized by a periodic sublattice of Ni-atom vacancies. These anomalous properties are evidence of a metal-insulator transition at low temperatures.

In this letter we report the results of the first study of the galvanomagnetic properties of intermetallic compounds with the formula RNiSn (R = Zr, Hf, Ti). The results show that a metal-insulator transition occurs in the spectrum of these compounds.

The isostructural compounds RNiSn and RNi_2Sn form in the ternary R-Ni-Sn systems, where R = Zr, Hf, Ti (Ref. 1). A distinctive feature of the crystal structure of RNiSn compounds in comparison with the compound RNi_2Sn is the presence of four vacancies of Ni atoms in each unit cell. The periodically positioned Ni vacancies form a vacancy lattice of cubic symmetry.

The RNiSn samples were prepared by smelting a stock material of the pure components (with a purity no worse than 99.99%) in an electric-arc furnace in an atmosphere of purified argon. The alloys were subjected to a homogenizing annealing in quartz cells at 800 °C. The composition and homogeneity were monitored with the

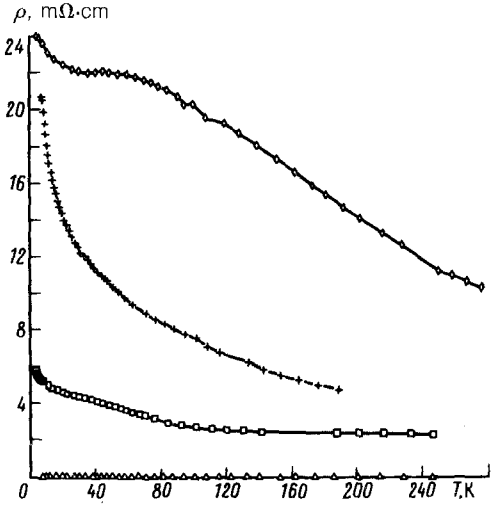

FIG. 1. Temperature dependence of the electrical resistivity $\rho(T)$ for various samples. ◇—HfNiSn; +—ZrNiSn; □—TiNiSn; △—$ZrNi_2Sn$.

help of diffraction patterns, which can be indexed quite successfully in a cubic crystallographic system.

The primary distinguishing feature of the polycrystalline samples of the RNiSn system which we studied is a resistivity which is unusually high for an intermetallic compound. At room temperature, it lies in the range 1–15 $m\Omega \cdot cm$, and as the temperature T is lowered, it reaches $\sim 10^2$ $m\Omega \cdot cm$ (Fig. 1). The vacancy-free compounds RNi_2Sn are typical metals, with a resistivity two or three orders of magnitude lower than that of RNiSn (Fig. 1). The anomalous properties of the RNiSn system cannot be a consequence of the appearance of microscopic cracks in the samples as the temperature is lowered, since the results are reproducible during repeated cycles of heating and cooling. In addition, it is found that the properties of the samples of a given compound, prepared by different methods (with different degrees of annealing, for example) may be quite different (Figs. 1 and 2). To determine the reasons for this situation, we studied the dependence of the electrical properties on the annealing time for two of the ZrNiSn samples, No. 1 and No. 2 (Fig. 2). We simultaneously used a computer to analyze the x-ray data from which we determined the extent and nature of the disorder of the lattice. It turned out that in the annealed ZrNiSn samples the Ni-atom vacancies are positioned strictly periodically, and in addition there is a certain extent ($\sim$10–30 at.%) of mutual substitution of the Zr and Sn atoms. In other words, the formula for the ZrNiSn must be written $(Zr_{1-x}Sn_x)Ni(Sn_{1-x}Zr_x)$ $(0.1 < x < 0.3)$. A change in the degree of disorder of the Zr and Sn sublattices strongly influences the $\rho(T)$ dependence. The maximum increase in $\rho(T)$ occurs for samples with the least disorder (Fig. 2).

For most of the $\rho(T)$ curves of the RNiSn samples with a monotonic increase in ρ with decreasing T, it is not possible to determine the functional dependence $\rho(T)$ accurately. At $T < 300$ K, at least, the dependence is not exponential. Furthermore, for

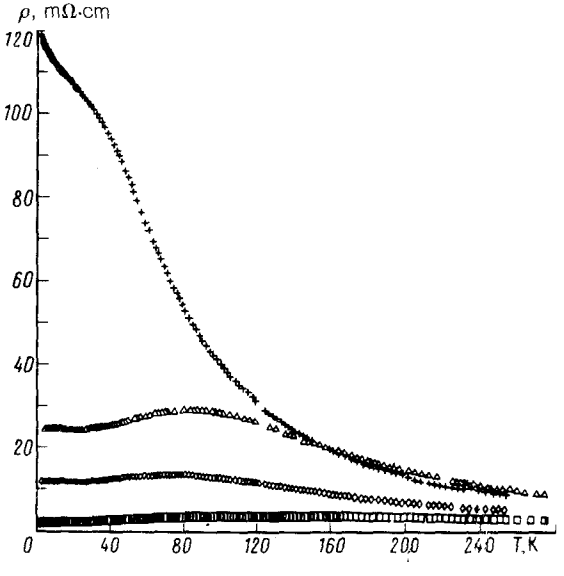

FIG. 2. Temperature dependence $\rho(T)$ for ZrNiSn sample No. 2 for various extents of annealing. □—Not annealed, 1— $x = 0.68 \pm 0.13$; +—168 h, 1— $x = 0.83 \pm 0.7$; ◇—340 h, 1— $x = 0.8 \pm 0.11$; △—670 h, 1— $x = 0.8 \pm 0.06$.

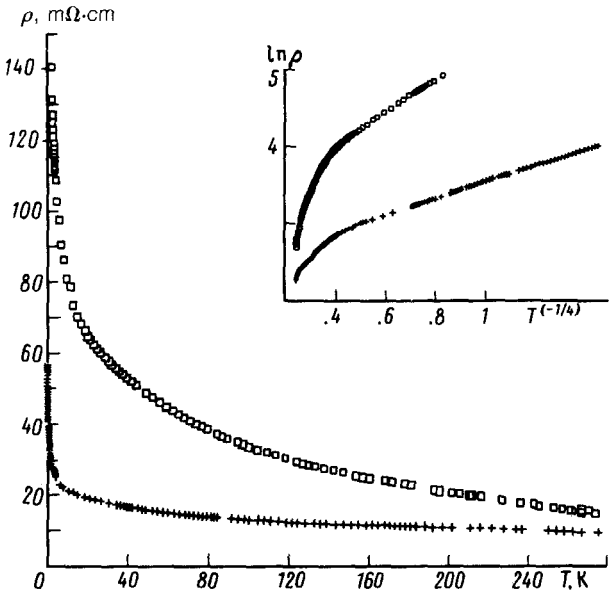

FIG. 3. Temperature dependence $\rho(T)$ for ZrNiSn sample No. 3 (+) and for a TiNiSn single crystal (□). The inset shows the onset of a Mott law in the coordinates $\ln\rho(T^{-1/4})$.

ZrNiSn sample No. 3, for which $\rho(T)$ does not reach saturation down to $T\approx 0.1$ K (Fig. 3), we find that below $T\approx 20$ K a Mott law[2] $\rho=\rho_0^*\exp(T_0/T)^{1/4}$ holds as the temperature is varied over more than two orders of magnitude (see the inset in Fig. 3). In the region in which the Mott law holds the magnetoresistance is positive, and it increases in magnitude as $T\to 0$. The carrier concentration estimated from the Hall coefficient lies in the range $\approx 10^{19}$–10^{20} cm^{-3} for the various RNiSn samples. The dielectric properties of the RNiSn systems cannot be linked with the opening of a gap at the point of a magnetic transition, since measurements of the magnetic properties revealed that these systems are Pauli paramagnets with $\chi_p\sim 10^{-4}$ msu/mole.

A study of the electrical properties of a TiNiSn single-crystal sample revealed that it also exhibits a conversion to a dielectric spectrum (Fig. 3), and a Mott law holds over the temperature range 1.8–40 K.

Fourier spectroscopy of ZrNiSn sample No. 3 and measurements of $\rho(T)$ up to 1000 K indicate that the electron-state density has minima in the region $E_g\approx 0.15$–0.4 eV, and the plasma frequency, $\omega_p\approx 400$ cm^{-1} correlates well with the electron density calculated from measurements of the Hall effect. On the whole, these results are evidence that the formation of a sublattice of Ni-atom vacancies in the RNiSn system leads to a sharp decrease in the electron-state density near E_F and to the localization of charge carriers at low temperatures.

Properties similar to the RNiSn properties, which we observed in the present experiments, have recently been found[3] in the UNiSn system, with the only distinction that in the UNiSn system the U atoms induce a low-temperature magnetic transition.

We wish to thank I. P. Zvyagin for a discussion on these results and A. I. Belogorokhov for assistance in the experiments.

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Translated by Dave Parsons