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Effect of Pressure on the Magnetic and Electrical Transition Point of the NiAs-Type NiS

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In order to study the nature of the first-order antiferromagnetic transition in NiS the electrical resistivity in the vicinity of the transition point has been investigated at the hydrostatic pressures up to 7 kbar. The transition has characteristics of semiconductive-metallic transformation. The transition point, observed at 230°K at atmospheric pressure, is lowered as the hydrostatic pressure is increased, with the rate $(dT_t/dP) = -(6.0 \pm 0.3) \text{ deg./kbar}$. The transition can be described in terms of the electronic rearrangement in *d*-orbitals of nickel atoms between localized-collective electronic states.

§1. Introduction

Some of the NiAs-like compounds are known to have various type of magnetic transitions. In a case of Ni-S system, Laffitte¹⁾ has shown by X-ray, pycnometric and magnetic measurements that the NiAs-type phase extends from Ni_{1.000}S to Ni_{0.943}S above 670°K. In the neutron diffraction patterns of NiS, Sparks and Komoto²⁾ have found an antiferromagnetic structure below 263°K, which consists of the moments ($2\mu_B$) pointing to the direction of the *c*-axis and coupling antiferromagnetically between the adjacent *c*-planes. Subsequently, they³⁾ have observed the absence of the angular dependence of a paramagnetic diffuse scattering, and have suggested that the localized moment may be lost at temperature above the transition point. It has also been considered from the discontinuous change in the lattice parameters, behaviours of the magnetic susceptibility and the sublattice magnetization, and the thermal hysteresis at the transition points that the transition is of a first-order transition.

In the present study the electrical resistivity in the vicinity of the transition temperature and the pressure effect on the transition point have been investigated in order to study the nature of transition.

§2. Experimental Methods

For the preparation of samples, the powders of nickel (99.9 percent purity) and sulfur (99.99 percent purity) were mixed together in the stoichiometric composition, and were doubly

sealed in silica tubes. The mixture was gradually heated up to 1000°K, and was kept at this temperature for three days. In order to obtain the NiAs-type phase, the powdered sample was melted at 1300°K, and was quenched from 1000°K. The polycrystalline ingot obtained, which had a golden luster, was used in the shape of $3 \times 3 \times 10 \text{ mm}^3$ for electrical resistivity measurement.

The sample was confirmed to be a single phase of the ordinarily NiAs-type structure with the lattice parameters of $a = 3.44 \text{ \AA}$, $c = 5.35 \text{ \AA}$ and with the magnetic susceptibility χ_0 of $2.4 \times 10^{-6} \text{ emu/g}$ at room temperature. These values are in good agreement with those of the stoichiometric NiS ($a = 3.439 \text{ \AA}$ and $c = 5.348 \text{ \AA}$, and $\chi_0 = 2.5 \times 10^{-6} \text{ emu/g}$) reported by Laffitte.¹⁾

The assemblies for electrical resistivity measurement at pressure are shown in Fig. 1. Hydro-

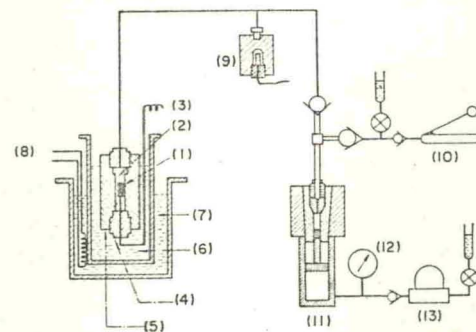


Fig. 1. The schematic diagram of the assemblies for electrical resistivity measurement at pressure. 1-specimen, 2-*n*-pentane, 3-six leads for current, potential probes and thermocouple, 4-pressure plug, 5-pressure vessel (2% Be-Cu alloy), 6-freezing mixture 7-water (for heating run), 8-heater leads, 9-manganin gauge, 10-hand pump, 11-pressure intensifier, 12-Bourdon gauge, 13-electric pump.

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static pressure up to 15 kbar was attained with an intensifier driven by an electric oil pump; the pressure was measured by observing the change in resistivity of a manganin coil. The pressure vessel of 2%Be-Cu alloy was cooled with solid CO₂-ethanol or liquid nitrogen for cooling runs, and heated with water in a double cryostat. Normal pentane was used as the transmitting fluid. The sample holder for electrical resistivity measurement at pressure has been described in the previous paper.⁴⁾ The measurement was carried out at the temperatures of 200~300°K.

§3. Experimental Results

The temperature dependence of magnetic susceptibility of the powdered sample, measured at the magnetic field $H=4.7$ koe and at the cooling rate of 2 deg./min., is shown in Fig. 2. The magnetic susceptibility has a value of the same order as usual Pauli paramagnetic susceptibility, and hardly depends on the temperature above 250°K. With lowering temperature the susceptibility increases abruptly by about 20 percent in the temperature range of 230 to 250°K. It remains nearly constant below 230°K. Although the transition is seen to extend over a considerable temperature interval, the increase of magnetic susceptibility is considered to correspond to the magnetic transition point.

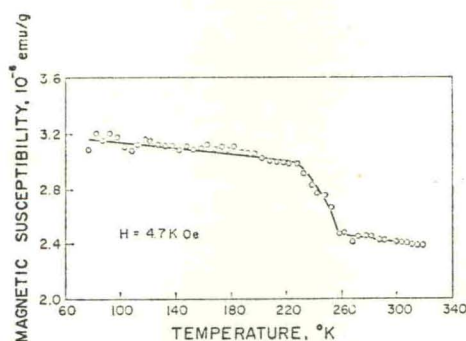


Fig. 2. Temperature dependence of the magnetic susceptibility of NiS.

The polycrystalline sample cooled at the temperatures below the transition point crumbled on rapid heating to room temperature. This is an evidence of anomalous, anisotropic volume change at the transition.

The temperature dependences of electrical resistivity of the polycrystalline ingot, measured at the cooling and heating rates of 1 deg./min., are shown in Fig. 3. In the first cooling run,

the specific resistivity ρ is observed to be 4×10^{-3} ohm-cm at room temperature and its temperature coefficient $d\rho/dT$, to be positive. A sharp change in electrical resistivity during cooling occurs at 230°K. The specific resistivity reaches the value of 7×10^{-4} ohm-cm and $d\rho/dT$ is observed to be negative below the transition point. In the subsequent heating run, a λ -shaped anomaly is observed at the transition point T_t^H , which is 4°K higher than that T_t^C in the cooling run. Finally the electrical resistivity recovers into the region of $d\rho/dT > 0$, but not to the initial value. The second run, made 48 hrs after the first run, shows the temperature behavior similar to the first heating run. The resistivity is linear on a plot of $\log \rho$ versus $1/T$ and yields an activation energy for conduction of $\sim 10^{-2}$ eV between 195 and 220°K.

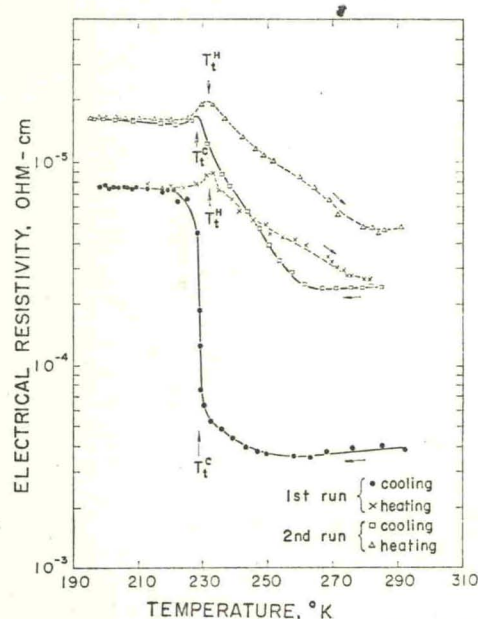
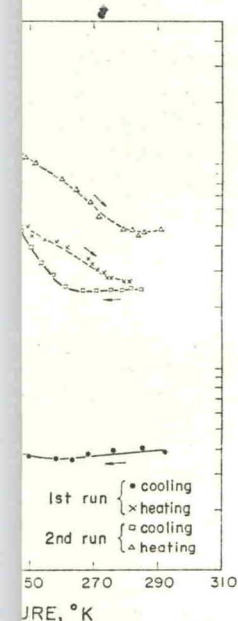


Fig. 3. Temperature dependence of electrical resistivity of NiS. The symbols T_t^C and T_t^H represent the transition points for cooling and heating runs, respectively.

Although the absolute value of resistivity can not be reproducible, the characteristics of a low-high resistivity transformation with the change in signs of $d\rho/dT$ and with the transition points T_t^C and T_t^H are reproducible, respectively. The variation in the transition point with the different samples is within 3°K. There is a little discrepancy in the transition temperature between the present and Sparks and Komoto's values.²⁾ The electrical resistivity measurement of NiS_{1+x}

is observed to be 4×10^{-5} and its temperature dependence is positive. A sharp change in resistivity occurs during cooling and occurs at the transition point. In the heating run, the resistivity reaches the value $d\rho/dT$ is observed to be a λ -shaped anomaly is observed on point T_t^H , which is T_t^C in the cooling run. The resistivity recovers into the initial value. After 3 hrs after the first run, the behavior similar to the first run is linear on a plot of $\ln \rho$ vs $1/T$. This yields an activation energy of 0.2 eV between 195 and



($x > 0$) shows considerably lower values of T_t^C than that of stoichiometric NiS. Such a discrepancy may be ascribed to the variation of chemical compositions. Since the anomalous point of the electrical resistivity is intrinsic character in the crystal and corresponds to that of the magnetic susceptibility data, it was used as the measure of the magnetic transition point.

The temperature dependence of the electrical resistivity of a sample (sample A) at 0, 0.8, 1.1 and 1.4 kbar are shown in Fig. 4. The detailed

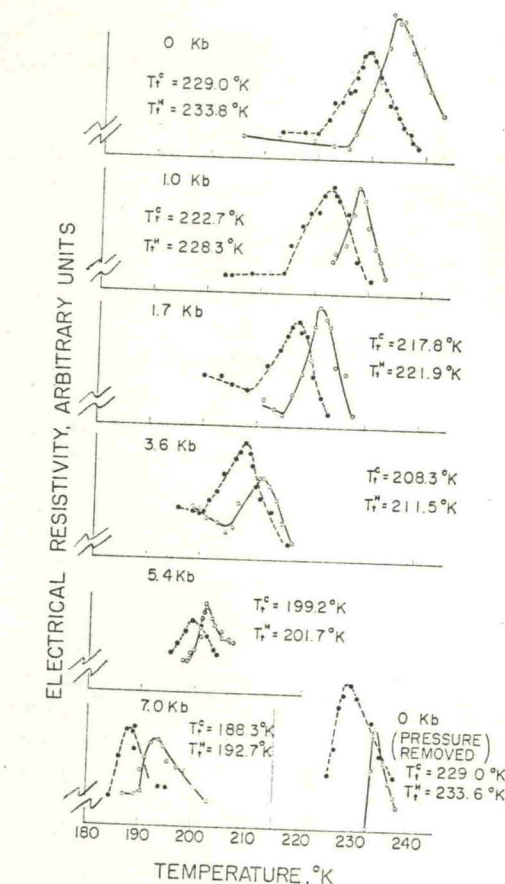
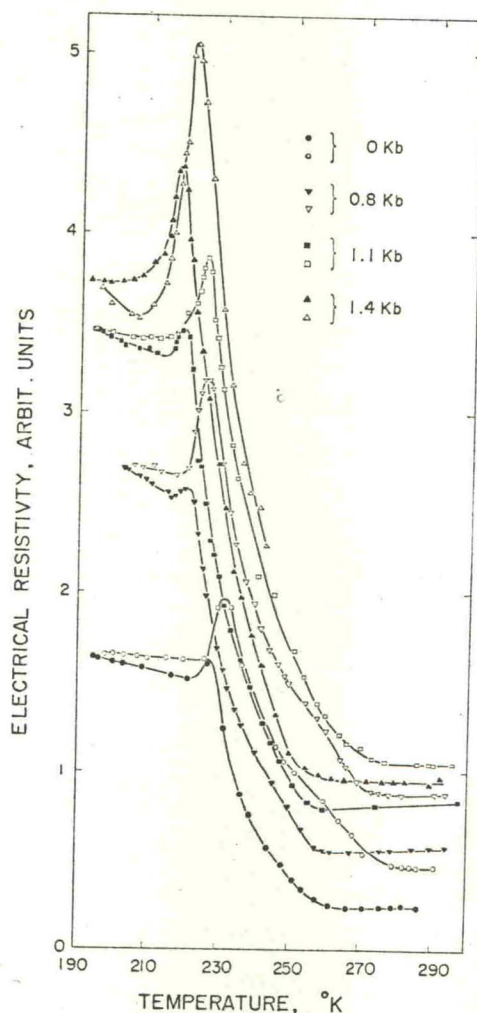


Fig. 5. Transition points of NiS at atmospheric and high pressures. Closed circles denote the cooling runs, and open, the heating runs.

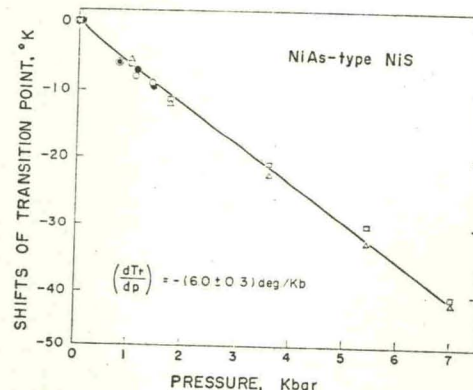


Fig. 4. Temperature dependences of the electrical resistivity of NiS at atmospheric and high pressure. Closed signs denote the cooling runs, and open, the heating runs.

Fig. 6. Pressure dependence of the magnetic transition point in NiS. The signs $\circ$ and $\bullet$ represent the cooling and heating runs, respectively, on sample A, and $\square$ and $\triangle$, on sample B.

value of resistivity can be characterized by a low-temperature transition with the change in the transition points T_t^C and T_t^H respectively. The variation of the transition point with the different pressure is shown in Fig. 6. There is a little discrepancy in temperature between the present measurement and Komoto's values.²⁾

measurements were made around the transition point of the other sample (sample B) at higher pressure up to 7 kbar. As shown in Fig. 5, the transition points T_t^C and T_t^H shift remarkably to lower temperatures with increase of pressure. A

slight thermal and pressure hysteresis in resistivity is observed during the several runs at high pressure. Since the reproducibility of the transition points are confirmed over the whole pressure range measured, the behavior of transition point

at pressure is considered to be an intrinsic character of the crystal. As shown in Fig. 6, the transition point is lowered linearly with increasing hydrostatic pressure, with the rate:

$$\left(\frac{dT_t^o}{dP}\right) = \left(\frac{dT_t^u}{dP}\right) = -(6.0 \pm 0.3) \text{ deg./kbar.}$$

§4. Discussions

It is revealed by present experiments that the stoichiometric NiAs-type NiS has an abrupt change in the electrical resistivity at the temperature corresponding to the first-order magnetic transition point. The magnetic transition has characteristics of semiconductive-metallic transformation in the electrical behaviors. The transition point shifts to lower temperatures with increase of hydrostatic pressure.

The nearly temperature-independent, small value of the paramagnetic susceptibility and a lower value of resistivity with $d\rho/dT > 0$ observed in this experiment above the transition point, and the absence of the angular dependence of a paramagnetic diffuse scattering and a large decrease in the lattice parameter corresponding to the disappearance of the sublattice magnetization reported by Sparks and Komoto^{2,3)} demonstrate that the *d*-electrons are collected into a partially filled, narrow *d*-band in the high temperature phase. The semiconductive character observed in present work, and the antiferromagnetic structure reported by Sparks and Komoto²⁾ below the transition point suggest that the *d*-electrons

localizes on Ni atoms in the lower temperature phase. Consequently, it is reasonable to suppose that the reduction of the interatomic spacings between Ni atoms stabilizes the collective *d*-band state than the localized states in NiS. It is remarkable that the first-order antiferromagnetic transition with a semiconductive-metallic phase change between localized-collective *d*-electronic states, observed in the compounds of less-than-half filled 3*d* elements such as V₂O₃ and Ti₂O₃,⁴⁾ is also found in a compound of the more-than-half filled elements.*

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* Note added in proof—Very recently Sparks and Komoto [Phys. Letters, 25A (1967) 398] have also reported that the magnetic transition in NiS is a semiconductor-metal transition.