Metal-to-Semiconductor Transition in Hexagonal NiS*

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Recent electrical resistivity measurements have shown that the hexagonal form of stoichiometric NiS exhibits an abrupt metal-to-semiconductor transition at 264°K. Neutron diffraction studies have shown that a first-order paramagnetic-to-antiferromagnetic transition also occurs at 264°K. No crystal lattice distortion is observed at the transition nor detected at 4.2°K, suggesting that this may be a transition of the kind considered by Adler and Brooks. The measured magnetic moment at 4.2°K is $1.66\pm0.08\ \mu_B$ and at 260°K it is $150.\pm0.10\ \mu_B$ indicating that the sublattice magnetization is within 10% of saturation immediately upon ordering. The neutron data also shown that no more than about 1% of the Ni atoms migrate to tetragonal interstitial sites on warming from 4.2°K to room temperature. Thus, Ni atom migration apparently plays no part in this transition. The powder magnetic susceptibility is 2.24×10^{-6} emu/g at 300°K and is virtually temperature-independent above the transition. χ increases abruptly at 264°K by about 15% and exhibits some field-cooling effects. Studies on the compounds Ni_XS, for $X=1.01$, 0.99, 0.97, and 0.94 show that excess sulfur lowers the transition temperature.

The metal-to-semiconductor transitions which occur in several of the oxides of the transition metals have been the subject of considerable experimental and theoretical attention for some years. Recently, Adler and Brooks[1] proposed a theory of such transitions in which they take as their model an intrinsic semiconductor with an energy gap separating the top of the valence band from the bottom of the conduction band and proceed to show that such a gap can arise either from an antiferromagnetic exchange interaction or from a crystal lattice distortion. From an examination[2] of the electrical, magnetic, and crystallographic properties of those oxides of vanadium and titantium which show a metal-to-semiconductor transition, it appeared that Ti_2O_3 was the only case in which antiferromagnetic ordering could be the mechanism responsible for the transition. The other oxides considered all exhibited a lattice distortion at the metal-to-semiconductor transition with no evidence of the simultaneous appearance of antiferromagnetic ordering. Some doubt, however, recently has been cast on the existence of antiferromagnetism in Ti_2O_3 by the neutron diffraction work of Kendrick *et al*,[3] which is in contradiction to the results of Abrahams,[4] and by the band model proposed by Van Zandt *et al*.[5] There has thus been some question as to the existence of a material exhibiting a metal-to-semiconductor transition arising from an antiferromagnetic exchange interaction as envisaged by Adler and Brooks.[1] We have recently examined the hexagonal form of NiS and found it to be a possible example of a material showing such an electrical transition originating from an antiferromagnetic interaction. In what follows, we give a brief resumé of the results of electrical and neutron scattering experiments plus some new information on the magnetic susceptibility and the effect of varying the sulfur content of this compound.

A powder neutron diffraction study[6] of the hexagonal nickel arsenide form of NiS disclosed an abrupt antiferromagnetic transition at 264°K. The magnetic structure deduced from the powder neutron data is that of a simple two-sublattice model in which the magnetic moments are coupled ferromagnetically within (001) layers, and moments on adjacent layers are coupled antiferromagnetically with the moments pointing as shown in Fig. 1. The *a*- and *c*-axis lattice parameters show an abrupt increase at the magnetic ordering temperature on cooling, and so does the volume of the unit cell. Hysteresis at the transition was observed both in the lattice parameter and the magnetic neutron intensity data, indicating the transition is first order. The magnetic moment from the neutron data at 4.2°K was found to be $1.66\pm0.08\mu_B$ and at 260°K, just four degrees below the transition, the moment is $1.50\pm0.10\mu_B$, indicating that the sublattice magnetization is within 10% of saturation immediately upon ordering. An apparent lack of para-

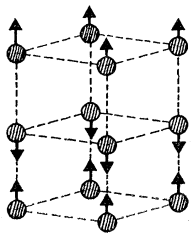

FIG. 1. Spin structure in hexagonal NiS. The sulfur atoms are not shown.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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magnetic diffuse scattering[7] above the transition indicates that the magnetic moment associated with the nickel atoms above the transition is small (less than about $0.5\mu_B$). This suggested that the electrical conductivity might show interesting behavior at the 264°K transition.

The electrical resistivity as a function of temperature was measured[8] for a compressed powder sample and the results are shown in Fig. 2. The cooling curve exhibits an abrupt change at 264°K in agreement with the neutron measurements. Above the transition the resistivity is linear in the temperature with a positive temperature coefficient indicative of metallic conductivity. An activation energy for conduction of 0.12 eV was calculated from the data in the region below the transition.

If this transition in NiS is an example of an antiferromagnetically induced semiconductor-to-metal transition as described by Adler and Brooks,[1] then there should be no lattice distortion associated with the transition. We have looked for evidence of distortion in the neutron diffraction data down to 4.2°K but have observed none. The c/a ratio is observed to increase abruptly on cooling through the transition but this can occur for a hexagonal crystal with no change in lattice symmetry.

There is the possibility of an entirely different mechanism operating in this structure. In MnBi, which also has the nickel arsenide-type structure, an abrupt magnetic transition has been observed. A neutron diffraction study[9] of this compound revealed that on warming an abrupt migration of about 10% of the Mn atoms occurs from the normal octahedral sites to tetragonal interstitial sites. The neutron intensity data for NiS shows, however, that no more than about 1% of the Ni atoms migrate to the interstitial sites on warming from 4.2°K to room temperature and no abrupt change is observed at the 264°K transition. It appears to be reasonable to conclude from this result that Ni atom migration plays no role in the observed transition.

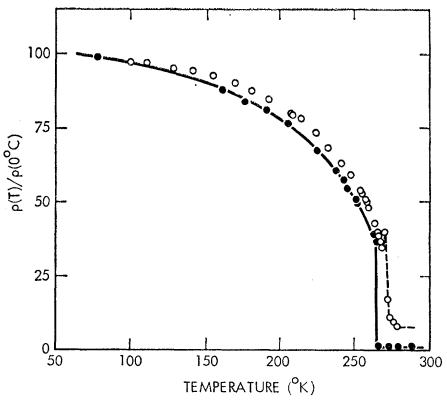

FIG. 2. Resistivity vs temperature for a compressed powder sample of NiS. The black circles are the cooling run and the open circles the subsequent warming run.

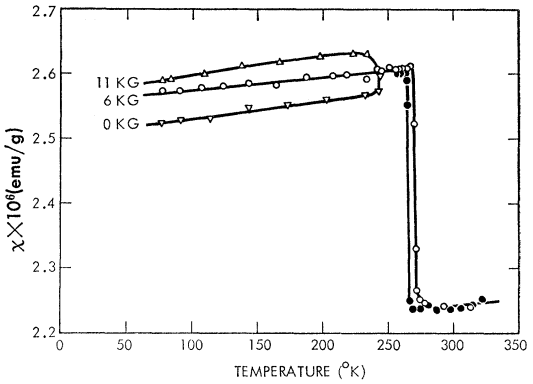

FIG. 3. Powder magnetic susceptibility vs temperature for hexagonal NiS. The black circles are the cooling run; the open circles and triangles are warming runs made after cooling the sample to 77°K in an applied field whose magnitude is shown at the left of the curves.

The powder magnetic susceptibility has been measured by the Gouy method from liquid nitrogen to room temperature and the results are shown in Fig. 3. The manner in which the curves were obtained is as follows: the sample was cooled directly to 77°K in three separate runs with applied external fields of 11, 6, and 0 kG. χ measurements were then made in each case on warming with a field of 6 kG. The transition at 264°K is sharp, about 3° wide, and occurs at the same temperature as the transitions observed in both the electrical and neutron measurements. Unfortunately, it is not possible to go to temperatures much above 300°K as the desired nickel arsenide form is stable only above 600°K and is obtained at low temperatures by quenching. In the limited temperature range examined above the transition, χ is small and appears to be virtually temperature independent, as one would anticipate for a material exhibiting metallic behavior and showing no evidence of an appreciable moment. At the transition, however, χ increases by only 15%. This is somewhat difficult to understand if a localized moment of the magnitude indicated by the neutron data exists below the transition; however, the magnitude of antiferromagnetic susceptibilities are notoriously difficult to calculate so no specific conclusion can be made here at this time. The three warming curves shown in the figure show that an external field has some effect on the susceptibility if applied during the cool-down through the transition. The effect is small and the significance is not understood. χ was found to be independent of the measuring field strength at 77°, 255°, and 300°K, indicating that

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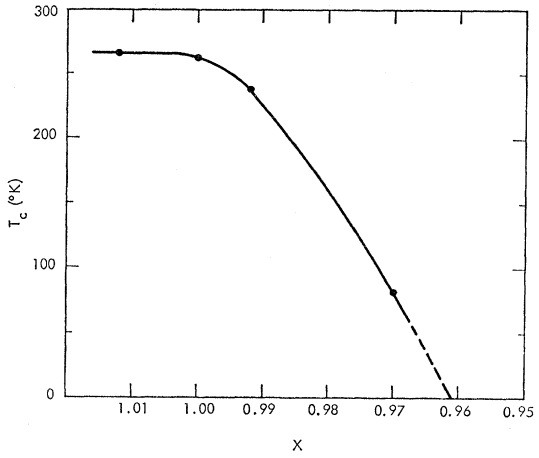

FIG. 4. The observed transition temperature T_c vs the composition X in Ni_XS.

no weak ferromagnetism is associated with the magnetically ordered state which could arise, for example, by a slight canting of the Ni moments.

A somewhat limited study of the effect of composition has been made by examining by neutron diffraction the series of compounds Ni_XS for $X=1.01$, 0.99, 0.97, and 0.94. The room-temperature lattice parameters as determined by x rays for these compounds are in good agreement with values reported in the literature.[10] The transition temperature decreases with increasing sulfur content as shown in Fig. 4. The results, both neutron and magnetic susceptibility, for $X=1.01$ are essentially identical to those for the stoichiometric, $X=1.00$, composition. The transitions observed in the $X=0.99$ and 0.97 compositions, however, are considerably broadened ($\sim 30°$K in width) as compared to $X=1.00$ and occur at distinctly lower temperatures. No transition was observed in the $X=0.94$ sample down to liquid-nitrogen temperatures.

As a final remark, the theory of such transitions does not appear to be entirely settled. Although we referred above only to the theory of Adler and Brooks,[1] Fröhlich[11] has recently proposed a theory, which has been applied by Hyland[12] to the vanadium oxides, in which Coulomb correlations between the conduction electrons play the dominant role and magnetic ordering is apparently incidental. It is not clear, as yet, whether Fröhlich's theory offers a satisfactory explanation of NiS or not.

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