

Hall effect and conductivity in pyrite NiS₂

Tineke Thio and J. W. Bennett

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

(Received 6 May 1994)

We report Hall-effect measurements on single crystals of antiferromagnetic pyrite-type NiS₂ ($T_N = 40$ K), in which the resistivity appears to show a metal-insulator transition at $T \approx 100$ K. Our transport measurements demonstrate that this transition is not intrinsic to the bulk: At low temperatures the transport is dominated by a metalliclike conduction at the surface, with carrier density $n_S \approx 5 \times 10^{14}$ cm⁻² and mobility $\mu_S \approx 1.3$ cm²/V s at $T = 0$. For $T > 100$ K the sample conductance is dominated by the bulk, which behaves like a doped semiconductor; the acceptorlike impurity states have binding energy $E_B = 80$ meV. The valence-band mobility is $\mu \approx 0.002$ cm²/V s.

I. INTRODUCTION

In the family of pyrite-type materials NiS_{2-x}Se_x a Mott-Hubbard metal-insulator transition occurs close to $x \approx 0.5$.^{1,2} The Se-rich compounds ($x > 1.0$) are paramagnetic metals. Between $x \approx 0.5$ and 1.0 magnetic correlations are observed in the metallic phase at low temperature.¹ The S-rich compounds ($x < 0.4$) order antiferromagnetically below $T_N = 40 - 50$ K; in these compounds the conductivity shows insulating behavior at high T . Surprisingly however, a metal-insulator transition appears to occur even in the antiferromagnetic phase: The resistance $R(T)$ shows a maximum which for the pure material NiS₂ occurs at $T \approx 100$ K; below this temperature $R(T)$ is metalliclike (that is, $dR/dT > 0$), even in the Néel state. Even more surprisingly, the Néel transition itself^{2,3} at $T_N \approx 40$ K is not apparent in $R(T)$ at all. It would be useful to have a measurement of the carrier density in order to study this intriguing temperature dependence; however, the Hall effect has not been previously reported, because it was found to be extremely small.^{4,5}

In this paper, we report transport measurements in single-crystal NiS₂, including the first measurement of the Hall effect. Our measurements show that in fact no metal-insulator transition occurs which is intrinsic to the bulk, but that at low temperatures the transport is dominated by a surface layer. The data agree well with a two-channel model which allows for contributions to the conductance and Hall effect from both the surface and the bulk. We find a surface carrier density $n_S \approx 5 \times 10^{14}$ cm⁻², corresponding to about one carrier per surface atom; the surface mobility at $T = 0$ is $\mu_S(0) \approx 1.3$ cm²/V s. For $T > 150$ K, the conductance (but not the Hall effect) is dominated by the bulk, which behaves like a semiconductor with acceptorlike impurities which have binding energy $E_B = 80$ meV. The valence band has mobility $\mu_B = 0.002$ cm²/V s. The two-channel conduction model accounts for an apparent discrepancy between the

activation energy of the conductivity and that of the Hall density.

II. EXPERIMENTAL DETAILS

Single crystals of NiS₂ were grown by the chemical vapor transport method using bromine as a transport agent.⁶ As starting material, NiS₂ powder was synthesized from 5-nines pure elements, with 5% excess sulfur, held at 700 °C for 72 h in evacuated quartz ampoules. 3 – 5 g of the powder was sealed in quartz ampoules of 12 – 19 mm diameter and 200 mm length, together with 50 – 100 ml Br₂ vapor at 20 °C. The ampoules were placed in a tube furnace at an average temperature $T_{av} = 700 - 800$ °C and a controlled gradient of 0.5 – 1.2 °C/cm, with the starting material at the hot end. Growth times varied from five days to six weeks, yielding single-crystals shaped like truncated octahedra with shiny (100) and (111) facets. The crystals were 3–7 mm long and up to 0.3 cm³ in total volume. Samples grown by this method are known to be sulfur deficient.⁷ The specific gravity of our crystals, measured by immersion techniques using methanol, is $\rho_m = 4.38 \pm 0.02$ g/cm³, which indicates⁷ that the composition of our crystals is NiS_y with $y = 1.92 \pm 0.02$ (there are 4% S vacancies). The lattice constant, measured by single-crystal x-ray diffraction,⁸ is $a = 5.688(2)$ Å, indicating⁷ $y = 1.92 \pm 0.04$, consistent with the density measurement.

The crystals were cleaved along (100) planes, into brick-shaped samples. This preparation method avoids surface damage from cutting or polishing. Electrical contacts were made using silver paint, in the geometry indicated in the inset of Fig. 1. The resistivity was measured with the current in a (100) direction; the Hall effect was measured in a five-probe configuration, in order to minimize the effects of magnetoresistance. The sample was mounted on a temperature-controlled holder and placed in the center of an Oxford superconducting magnet; the transverse voltage V_y was measured using a Linear Re-

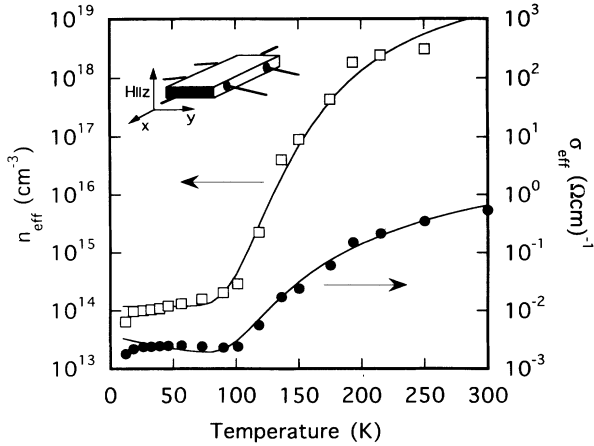


FIG. 1. Temperature dependence of n_{eff} (open squares) and σ_{eff} (closed circles, right-hand scale). The solid lines are fits to Eqs. (2) and (5). The inset shows the measurement geometry.

search LR-400 resistance bridge, at magnetic fields up to ± 10 T. At high temperatures, where the Hall coefficient is very small, V_y was averaged over repeated sweeps of the magnetic field.⁹

III. RESULTS

In order to investigate the possibility of surface conduction, two brick-shaped samples were cleaved from adjacent sites of the same crystal. The sample dimensions transverse to the current were L_y, L_z ; the distance between voltage leads was L_x . For bulk conduction, the conductivity is found from the conductance g_x from $\sigma_B = g_x L_x / L_y L_z$; for surface conduction it is $\sigma_S = g_x L_x / 2(L_y + L_z)$. The geometrical factor $L_y L_z / L_x$ in the two samples were different by a factor 6, whereas $2(L_y + L_z) / L_x$ were different by a factor 1.2. For $150 < T < 300$ K the resistances of these two samples differed by a factor ~ 6 , scaling as a bulk resistance. However, below $T \sim 100$ K the resistances were equal to within 20%. Similar results were obtained in several pairs of samples prepared in the same way.

Figure 1 shows the temperature dependence of the effective conductivity of one of the samples, $\sigma_{\text{eff}}(T) = g_x L_x / L_y L_z$, which is similar to that reported in the literature.^{4,6} For $150 < T < 300$ K, $\sigma_{\text{eff}}(T)$ is thermally activated with an activation energy $E_\sigma = 80 \pm 3$ meV. At $T \approx 100$ K $\sigma_{\text{eff}}(T)$ has a minimum; below 100 K it is weakly temperature dependent with metalliclike behavior: $d\sigma/dT < 0$, and the magnitude of σ_{eff} is sample dependent, as discussed above.

In the Hall effect measurements, the transverse voltage V_y can be described as the sum of a part which is symmetric in magnetic field H , and an antisymmetric part. The symmetric part of V_y is due to residual magnetoresistance, which is of order 1% at $H = 10$ T. The antisymmetric part of V_y is found to be linear in magnetic field to $H = 10$ T: this we identify as the Hall voltage. The Hall coefficient is positive in the entire temperature

range of the measurement. Figure 1 shows (open squares) the temperature dependence of the effective Hall density n_{eff} , computed, like σ_{eff} , as if all the transport occurred in the bulk; we discuss this issue in detail below. The Hall coefficient spans more than four orders of magnitude between 10 and 250 K. Below 100 K it is weakly T dependent; for $120 < T < 250$ K it is thermally activated, like the conductivity, but with a larger activation energy $E_H = 0.14 \pm 0.03$ eV. The effective carrier mobility $\mu_{\text{eff}} = \sigma_{\text{eff}} / en_{\text{eff}}$ is plotted in Fig. 2 as a function of temperature. At the lowest T , μ_{eff} is higher than that at high temperatures by a factor of nearly 1000.

IV. DISCUSSION

Since the two samples measured in the geometry dependence experiment originate from adjacent parts of the same crystal, we assume that they are identical except in their geometries. Their conductances scale as a bulk conductance at high T : $g_B \sim L_y L_z / L_x$, whereas at low T they scale as a surface conductance: $g_S \sim 2(L_y + L_z) / L_x$. The geometry dependence of the conductance thus gives compelling evidence that in NiS₂ the maximum in $\rho(T)$ is not intrinsic to the bulk material, but that below $T \approx 100$ K the current is carried at the surface.

In the following, we discuss the transport properties of a sample which has significant surface conduction.¹⁰ Consider a parallelepiped sample of dimensions L_x, L_y, L_z , with a magnetic field in the z direction, and with current i_x applied in the x direction. The sample can be thought to consist of three layers: the bulk and two surface layers. In each layer, labeled i , the x, y components of the current density and the electric field are related by the usual relation $\mathbf{j}_i = \overset{\leftrightarrow}{\sigma}_i \mathbf{E}$; where the conductivity tensor is given by

$$\overset{\leftrightarrow}{\sigma}_i = \sigma_i \begin{pmatrix} 1 & \omega_i \tau_i \\ -\omega_i \tau_i & 1 \end{pmatrix}; \quad (1)$$

here $\sigma_i = n_i e \mu_i$ is the zero-field conductivity, $i = B, S$

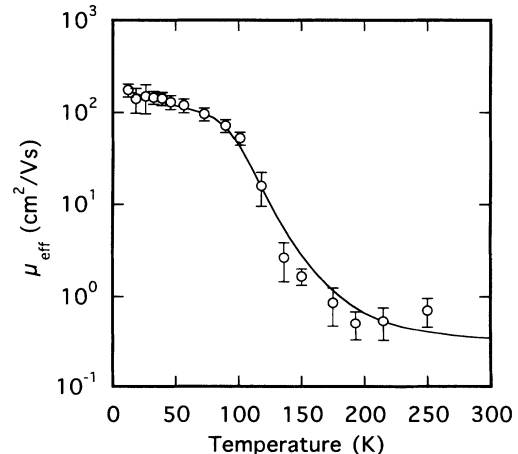


FIG. 2. Temperature dependence of μ_{eff} . The solid line is a fit to Eq. (6).

indicate the bulk and the surface, respectively; $\omega_i = eH/m_i^*c$ is the cyclotron frequency (m_i^* is the effective mass), and τ_i the scattering time of the carriers in each layer. [Note that n_S (cm^{-2}) is a surface carrier density, while n_B (cm^{-3}) is a bulk density]. We consider a flat thin sample ($L_x, L_y \gg L_z$). The effective conductivity is found from the total conductance $g_x = g_B + 2g_S$:

$$\sigma_{\text{eff}} = \frac{g_x L_x}{L_y L_z} = \sigma_B + \frac{2\sigma_S}{L_z}; \quad (2)$$

this is the quantity plotted in solid circles in Fig. 1.

The transverse fields are found from

$$\begin{aligned} \sigma_B E_y &= -\omega_B \tau_B \sigma_B E_x + j_{yB}, \\ \sigma_S E_y &= -\omega_S \tau_S \sigma_S E_x + j_{yS}. \end{aligned} \quad (3)$$

Here j_{yB} and j_{yS} are the y components of the current densities of the bulk and the surface, respectively. The assumption that the electric fields E_x and E_y in the bulk and at the surface are equal is correct at distances larger than L_z from the edges, so this is a good approximation for the flat thin sample of this model. In steady state, the total transverse current vanishes:

$$L_z j_{yB} + 2J_{yS} = 0. \quad (4)$$

From the Hall voltage, determined by Eqs. (3) and (4), one finds the effective Hall density, also computed as if all the transport occurred in the bulk:

$$\frac{1}{n_{\text{eff}}} = \frac{\sigma_B^2/n_B^2 + 2\sigma_S^2/n_S L_z}{(\sigma_B + 2\sigma_S/L_z)^2}, \quad (5)$$

$n_{\text{eff}}(T)$ is plotted as the open squares in Fig. 1. The effective mobility is

$$\mu_{\text{eff}} = \frac{\sigma_{\text{eff}}}{n_{\text{eff}} e} = \frac{n_B \mu_B^2 + 2n_S \mu_S^2 / L_z}{n_B \mu_B + 2n_S \mu_S / L_z}. \quad (6)$$

Note that σ_{eff} , n_{eff} and μ_{eff} contain a geometrical factor (L_z) in the surface contributions.

We fit our data to the two-channel conduction model, assuming the simplest conduction mechanism in the bulk and in the surface layer: The data is consistent with metalliclike conduction at the sample surface, and bulk conduction by carriers thermally activated from an impurity band close to the valence band. At high T , the temperature dependence of the conductivity suggests that the carrier density n_B is thermally activated with a single activation energy E_B : $n_B(T) = n_{B0} \exp(-E_B/kT)$; we assume the mobility μ_B to be temperature independent.

In the metallic region between 10 and 60 K, μ_{eff} decreases by 30%. Accordingly, we use a temperature-dependent mobility $\mu_S(T) = e/m_S^* \nu$, where we assume the scattering rate $\nu(T)$ to have the simplest temperature dependence: the sum of a constant and a term which varies linearly with temperature, as is appropriate for, e.g., electron-phonon scattering. For such a case the surface mobility can be written: $\mu_S(T) = [(\mu_S(0))^{-1} + C_\mu T]^{-1}$. We further assume that the surface carrier den-

sity n_S is temperature independent.

Fits to this model, using Eqs. (2), (5), and (6), and with $L_z = 0.6$ mm, are shown as the solid lines in Figs. 1 and 2. Our simple model fits the data very well over the entire temperature range of the measurement. The fits yield the following parameters: The high-temperature bulk mobility is $\mu_B = (2.0 \pm 0.3) \times 10^{-3} \text{ cm}^2/\text{Vs}$, consistent with the upper limit $\mu < 0.5 \text{ cm}^2/\text{Vs}$ found in Refs. 4 and 5. The activation energy of the bulk carrier density is $E_B = 80 \pm 5 \text{ meV}$, identical to E_σ ; the prefactor is $n_{B0} = (5 \pm 2) \times 10^{22} \text{ cm}^{-3}$. At the surface the carrier density is $n_S = (5 \pm 2) \times 10^{14} \text{ cm}^{-2}$, with a zero-temperature mobility $\mu_S(0) = 1.3 \pm 0.2 \text{ cm}^2/\text{Vs}$ and $C_\mu = (9 \pm 2) \times 10^{-3} \text{ Vs/cm}^2 \text{ K}$. The values for the surface conduction are reported for one sample only; they are expected to depend on the details of the surface quality, and indeed they vary between crystals grown in different runs.

We find that the two-channel conduction model provides a very good description of the data. Indeed, if the low- T conductivity occurred in the bulk, it would be difficult to explain why a very small density of carriers at low T should have a much higher mobility than those observed at higher T . Furthermore, the surface carriers are insensitive to the bulk magnetic ordering, which explains why the Néel transition is not apparent in the temperature dependence of the effective conductivity. The presence of a conducting surface layer is probably the reason why the optical reflectivity is independent of photon energy E_ϕ for $0.05 < E_\phi < 4 \text{ eV}$, whereas in transmission an absorption edge at $E_\phi = 0.3 \text{ eV}$ is observed, which is attributed to absorption in the bulk.^{4,5}

The model explains the apparent discrepancy of the activation energies E_B and E_H : By $T = 200 \text{ K}$ the contribution of σ_S to the total conductivity is negligible. However, even at $T = 250 \text{ K}$ the Hall coefficient is still influenced by the surface conduction, even though $n_S \ll n_B$, since the densities are weighted by μ^2 [see Eqs. (5) and (6)], and μ_S is larger than μ_B by a factor of order 100; E_H , therefore, has no physical meaning. The model predicts that $\sigma_{\text{eff}}(T)$ and $n_{\text{eff}}(T)$ have the same activation energy above 300 K. We show no data to support this prediction, because above room temperature the Hall coefficient becomes immeasurably small.

Since the Hall coefficient is positive, the results at high T suggest transport by carriers which are thermally excited from acceptorlike states into the valence band. This is consistent with measurements of the Seebeck coefficient S ,⁴ which is positive for $100 < T < 500 \text{ K}$ (for $T < 100 \text{ K}$, the measurement of S is presumably also influenced by the surface conduction). The binding energy of the acceptors is $E_B = 80 \text{ meV}$. In the present work, the Hall density was measured to $T = 250 \text{ K}$; above this temperature the conductivity continues to increase with the same activation energy for another decade, before showing evidence of saturation.⁵ We therefore estimate the density of acceptors to be $n_A \sim 4 \times 10^{21} \text{ cm}^{-3}$. A possible candidate for such a high density of acceptors is the 4% sulphur vacancies;⁷ however, very little is known about the microscopic properties of these defects. The Hall effect measurements indicate that the valence band has a

temperature-independent mobility $\mu_B = 0.002 \text{ cm}^2/\text{V s}$; this is a small mobility, even for a valence band dominated by nickel d states,¹¹ and indicates either a very short scattering time, or a large effective mass.

It is unusual for a semiconductor surface to be metallic. Although the dangling bonds at the semiconductor surface are partially filled, often the surface is found to be nonmetallic, through, e.g., surface reconstruction.¹² Indeed, the surface of NiS₂ is not a good metal, the mobility being only $\mu_S \sim 1 \text{ cm}^2/\text{V s}$; but it is metalliclike, in that $dR/dT > 0$. In contrast, high surface conduction has been observed in some semiconductors such as¹³ ZnO and InSb,¹⁴ with surface mobilities $\sim 10^4 \text{ cm}^2/\text{V s}$. In NiS₂, the carriers at the surface and in the bulk have the same sign, but in (Hg,Cd)Te p -type conduction in the bulk is sometimes masked by electrons at the surface, which have a much higher mobility than the holes in the bulk.¹⁵ The carrier density observed in NiS₂ is quite high, especially when compared to that found in heterojunction interfaces, but not unprecedented: In ZnO surface densities $\sim 2 \times 10^{14} \text{ cm}^{-2}$ have been achieved by He bombardment. In NiS₂, $n_S = (5 \pm 2) \times 10^{14} \text{ cm}^{-2}$ corresponds to roughly one carrier per surface atom at the (100) face (the atomic surface density is $N_{\text{at}} = 6 \times 10^{14} \text{ cm}^{-2}$ for 2Ni, 4S atoms per surface unit cell). It is possible that the dangling bonds at the surface do not reconstruct but form a metallic p -bonding band. Alternatively, a high

density of sulfur vacancies can make the surface nickel rich and therefore metallic.

V. CONCLUSION

In summary, we have measured the conductivity and Hall effect in single-crystal NiS₂. The temperature dependence of the transport properties are modeled to that of a sample with significant contributions to the conduction from both the bulk and the surface. The model fits the data well at all temperatures $10 < T < 300 \text{ K}$. At low temperature the sample conductance is dominated by metalliclike conduction at the surface, with a carrier density $n_S = 5 \times 10^{14} \text{ cm}^{-2}$ and a $T = 0$ mobility $\mu_S(0) = 1.2 \text{ cm}^2/\text{V s}$. The bulk conductivity, which dominates the sample conductance at high temperatures, is carried by holes which are thermally excited from an acceptor band with binding energy $E_B = 80 \text{ meV}$. The carrier mobility in the valence band is $\mu_B = 0.002 \text{ cm}^2/\text{V s}$.

ACKNOWLEDGMENTS

We gratefully acknowledge R.C. Haushalter's advice on the crystal growth, as well as useful discussions with P.A. Wolff and N.S. Wingreen.

¹ J.A. Wilson, in *The Metallic and Non-metallic States of Matter*, edited by P.P. Edwards and C.N.R. Rao (Taylor and Francis, London, 1985), Chap. 9, p. 215.

² S. Ogawa, *J. Appl. Phys.* **50**, 2308 (1979).

³ T. Miyadai *et al.*, *J. Phys. Soc. Jpn.* **38**, 115 (1975).

⁴ P. Kwizera, M.S. Dresselhaus, and D. Adler, *Phys. Rev. B* **21**, 2328 (1980).

⁵ A.K. Mabatah *et al.*, *Phys. Rev. B* **21**, 1676 (1980).

⁶ R.J. Bouchard, J.L. Gillson, and H.S. Jarrett, *Mater. Res. Bull.* **8**, 489 (1973).

⁷ G. Krill *et al.*, *J. Phys. C* **9**, 761 (1976).

⁸ T.R. Thurston (unpublished).

⁹ J.W. Bennett and T. Thio, in *SEAM'93 Conference Proceedings, Boston, MA, 1993* (Mac Sci Tech, Worcester, MA, 1994).

¹⁰ R.L. Petritz, *Phys. Rev.* **110**, 1254 (1958).

¹¹ G. Krill and A. Amanou, *J. Phys. Chem. Solids* **41**, 531 (1980).

¹² D.J. Chadi, *J. Vac. Sci. Technol. A* **5**, 834 (1987).

¹³ M. Nitzan, Y. Grinshpan, and Y. Goldstein, *Phys. Rev. B* **19**, 4107 (1979).

¹⁴ E.W. Kreutz, *Phys. Status Solidi A* **40**, 415 (1977).

¹⁵ L.F. Lou and W.H. Frye, *J. Appl. Phys.* **56**, 2253 (1984).