[3]E. W. Fenton, J.-P. Jan, A. Karlsson, and R. Singer, Phys. Rev. 184, 663 (1969).
[4]V. Chopra, R. K. Ray, and S. M. Bhagat, Phys. Status Solidi (a) 4, 205 (1971).
[5]V. N. Kopylov and L. P. Mezhov-Deglin, Zh. Eksp. Teor. Fiz. 65, 720 (1973) [Sov. Phys. JETP 38, 357 1974)].
[6]S. M. Cheremisin, Zh. Eksp. Teor. Fiz. 65, 1564 (1973) [Sov. Phys. JETP 38, 779 (1974)].
[7]K. Anagnostopoulos and J. E. Aubrey, J. Phys. F 6, L181 (1976).
[8]R. Hartman, Phys. Rev. 181, 1070 (1969).
[9]C. A. Kukkonen and P. F. Maldague, Phys. Rev. Lett. 37, 782 (1976).
[10]C. A. Kukkonen and P. F. Maldague, J. Phys. F 6, L301 (1976).
[11]J. L. Imes, G. L. Neiheisel, and W. P. Pratt, Jr., J. Low Temp. Phys. 21, 1 (1975).
[12]E. L. Stone, M. D. Ewbank, J. Bass, and W. P. Pratt, Jr., Phys. Lett. 59A, 168 (1976).
[13]C. Uher, J. Phys. E 7, 245 (1974).
[14]C. Uher and W. P. Pratt, Jr., Bull. Am. Phys. Soc. 22, 333 (1977).
[15]At the conclusion of this work, we became aware of an independent observation of this deviation for a commercially available Bi single crystal above 1.1 K (C. Kukkonen and K. F. Sohn, private communication).
[16]V. S. Edelman, Adv. Phys. 25, 555 (1976).
[17]E. H. Sondheimer, Proc. Phys. Soc. London, Ser. A 65, 561 (1952).
[18]The difference between the predictions of the Bloch-Grüneisen formula and an extrapolation of the T^2 resistivity variation between 0.3 and 0.7 K is only about $3\times10^{-9}\ \Omega$ cm, even at temperatures as high as 1 K. Unless the measurements are done with a much better precision than 1%, one could not distinguish between the two mechanisms.
[19]Since Eq. (1) is presumed valid only at the lowest temperatures, the agreement between predictions of Eq. (1) and the data for single-crystal samples can be improved by making a fit to the data at lower temperatures, say, below 0.6 K. As a consequence, $\theta_D{}^*$ is reduced by about 20%. We have also attempted to include the anisotropy of the Bi Fermi surface in the electron-phonon scattering, along the lines suggested by Cheremisin (Ref. 6). Below 1 K we have done a computer fit to the expression

$$\Delta\rho = A\left(\frac{T}{\theta_{\min}{}^*}\right)^5 \int_0^{\theta_{\min}{}^*/T} \frac{x^5\,dx}{(e^x-1)(1-e^{-x})} + B\left(\frac{T}{\theta_{\min}{}^*}\right)^n \int_{\theta_{\min}{}^*/T}^{\theta_{\max}{}^*/T} \frac{x^n\,dx}{(e^x-1)(1-e^{-x})},$$

where $\theta_{\min}{}^*$ and $\theta_{\min}{}^*$ are temperatures corresponding to the minimum and maximum dimensions of the Fermi surface, and n is an integer. We have tried $n = 2, 3$. However, we were unable to achieve a significant improvement of the fits to the data below 1 K unless the coefficient B was chosen to be an order of magnitude smaller than the coefficient A.

Anomalous Electrical Transport Properties of $Ni_{1-x}Co_xS_2$

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We report results of electrical conductivity and thermoelectric power measurements on $Ni_{1-x}Co_xS_2$ ($0 \le x \le 0.12$) in the temperature range 77 K$<T<$ 600 K. When analyzed on the basis of conventional one-electron theories, these results are difficult to explain. However, the measurements can be quantitatively interpreted in terms of a model involving polaron transport in highly correlated, narrow energy bands associated primarily with the transition-metal cations.

The transport properties of the 3*d* transition-metal dichalcogenides having the pyrite structure have been intensively studied, but are still incompletely understood.[1,2] Previous workers have inferred an energy-level scheme in which the levels relevant to transport form a narrow antibonding band associated primarily with the 3*d* e_g states of the metal cations.[1] To explain the semiconducting properties of NiS_2, it has been speculated that NiS_2 is a Mott insulator, that is, insulating as a result of strong interelectronic correlations in this narrow band.

In this Letter, we present experimental results of transport measurements on the alloys

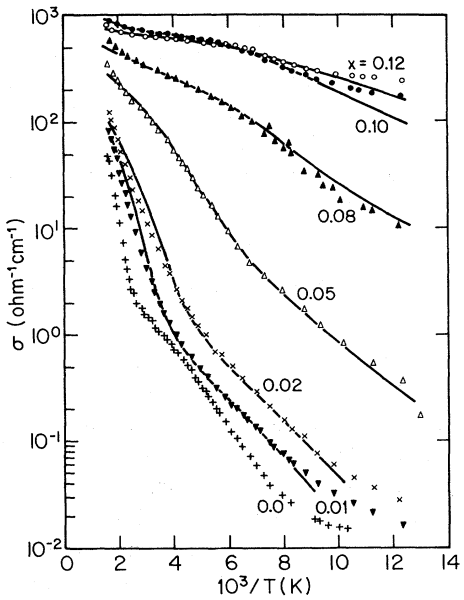

FIG. 1. Electrical conductivity vs $10^3/T$ for $Ni_{1-x}Co_xS_2$ ($0 \leq x \leq 0.12$). The solid lines were calculated from the model described in the text.

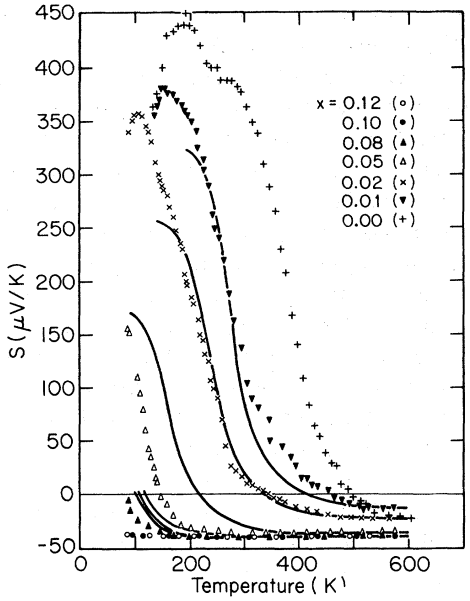

FIG. 2. Thermoelectric power vs temperature for $Ni_{1-x}Co_xS_2$ ($0 \leq x \leq 0.12$). The solid lines were calculated from the model described in the text.

$Ni_{1-x}Co_xS_2$ ($0 \leq x \leq 0.12$) which strongly support this suggestion. We shall demonstrate how a simple model involving correlation-split bands can account for the complex behavior observed.

Single crystals were grown by a chemical vapor transport technique using bromine as the transport agent.[3] The Co concentrations were verified by x-ray fluorescence measurements. Electrical conductivity measurements were made using the four-probe Van der Pauw method. The thermoelectric power measurements were made using standard heat-pulse techniques with the thermocouples electrically bonded to the sample.[4]

The results of conductivity and thermoelectric power measurements made on $Ni_{1-x}Co_xS_2$ ($0 \leq x \leq 0.12$) are shown in Figs. 1 and 2. Our data for undoped NiS_2 ($x = 0$) agree with results reported by Kautz *et al.*[5] In the following summary, we emphasize those features that are difficult to explain collectively with conventional one-electron band theory. For the measured range of x, the room-temperature conductivities vary from 1 to 10^3 $(\Omega\ \mathrm{cm})^{-1}$. At higher temperatures, the conductivities tend to a common maximum. In general agreement with earlier results,[1,5,6] the conductivities are thermally activated. We note, however, that our $Ni_{0.88}Co_{0.12}S_2$ single crystals exhibit semiconducting properties in the temperature range $90\ \mathrm{K} < T < 600\ \mathrm{K}$, contrary to the findings of Ogawa, Waki, Teranishi[6] for polycrystalline samples. The activation energies and the total range of conductivity values decrease with increasing x. For the range $x \geq 0.05$, the experimental conductivity shows three distinct temperture regions; in the low- and high-temperature regions, the activation energies are equal, and lower than that at intermediate temperatures. The "saturation" temperature (defined as the temperature above which the activation energy decreases to its smaller, high-temperature value) is a decreasing function of Co concentration.

For samples with $0.01 \leq x \leq 0.05$, the thermoelectric power increases with increasing T from a small, positive value near 77 K, to a large, positive maximum at intermediate T, and then decreases to a relatively small, negative, and *temperature-independent* value at high T. The magnitude and location of the peak and the temperature at which the thermopower changes sign are all decreasing functions of x. In the range $0.08 \leq x \leq 0.12$ and $T > 100$ K, the thermopower is negative (with magnitude $\simeq 40$ μV/K) and T independent.

The observed behavior can be explained in terms of a narrow conduction band split by strong electronic correlations. In NiS_2, the relevant band is associated primarily with the transition-metal e_g levels, well-separated from both a lower, filled, nonbonding (t_{2g}) band and a higher, empty, antibonding band.[1] The e_g band contains

four states per transition-metal ion, and, for pure NiS_2, is exactly half-full. Hubbard[7] has shown that when the electrons in a narrow energy band are strongly interacting, the pseudoparticle energy spectrum splits into two bands. We take the bandwidth to be the smallest energy in the model, so that the band gap is simply the electron correlation energy U_0. In NiS_2, the lower band is then full, the upper empty, thus explaining why NiS_2 is semiconducting. Co enters the lattice substitutionally for Ni and, hence, does not markedly perturb the crystal structure or the energy-level scheme. However, since Co^{2+} has one fewer electron than Ni^{2+}, the addition of Co continuously changes the occupancy of the isolated, correlation-split e_g bands.[1] Optical data[5] on pure NiS_2 show that the energy gap decreases linearly with temperature as $U(T) = U_0 - \alpha kT$. We assume that such a relationship persists in the alloy system. As a result, we can distinguish three temperature regimes. At low temperatures ($kT \ll U$), the bands are well separated, and electrical conduction is dominated by a small, fixed number of holes in the lower band. At higher temperatures ($kT \simeq 0.1U$), the number of carriers in both bands increases as $\exp(-U/2kT)$. The energy gap collapses totally at $T = U_0/\alpha k$. Above this temperature, the gap is taken to be exactly zero, which results in conduction dominated by a large, fixed number of electrons in a single, nearly half-filled band.

The dc conductivity σ of an extrinsic narrow-band semiconductor was first calculated by Bari.[8] He found that the number of excited carriers is given by

$$n(T) = n_0(T)\frac{4\exp(\epsilon_F/kT)\{1+\exp[(2\epsilon_F - U)/kT]\}}{Z^2}, \quad (1)$$

where ϵ_F is the Fermi energy and Z is the single-site grand partition function, both of which depend on Co concentration.[9] [$n(T)/n_0(T)$ is the fraction of site pairs permitting dc electron transfer within the pair, and $n_0(T)$ is a slowly varying function of temperature arising from the statistical sum over site configurations.] We assume that the carriers form small polarons with a mobility given by

$$\mu(T) = \mu_0(T)\exp(-E_H/kT), \quad (2)$$

where E_H is half the polaron binding energy and $\mu_0(T)$ is a slowly varying function of T. The thermoelectric power of a Hubbard insulator has been calculated by Bari[8] and by Beni.[10] For the case of hopping conduction, we must add to their expressions a temperature-independent contribution of the form, $-k\alpha'/e$, where α' is the change in entropy of an ion due to the presence of an electron, as discussed by Heikes.[11] The total thermopower, S, is then given by

$$S = -\frac{1}{eT}\left(\frac{U}{1+\exp[(U-2\epsilon_F)/kT]} - \epsilon_F\right) - \frac{k\alpha'}{e}. \quad (3)$$

Using Eqs. (1) and (2), we have generated a family of conductivity curves for the Co concentrations studied experimentally. Values for the zero-temperature band gap (U_0), the temperature coefficient of band collapse (α), and the hopping energy (E_H) were chosen to best fit the data.

The success of the model is demonstrated in Fig. 1. Note particularly that the theory reproduces well the decrease in number of decades spanned by the conductivity as x increases. This span is independent of the adjustable parameters. The model further explains the equal activation energies observed for those temperature ranges where a fixed number of carriers contributes to conduction ($kT/U \ll 1$ and $kT/U \gg 1$). The high-temperature "saturation" points of the conductivity are well fitted. The values chosen for U_0, α, and E_H are smoothly decreasing functions of Co concentration. The zero-temperature gap and hopping energy vary, respectively, from about 300 and 50 meV at $x = 0.01$ to about 50 and 10 meV at $x = 0.12$. The values of α used are very near the value of 4.7 obtained from optical absorption experiments on pure NiS_2.[5] In order to fit the absolute conductivity, it was necessary to vary as a function of x the infinite-temperature mobilities, but only by less than a factor of 5 over the entire range of compounds. The values of these infinite-temperature mobilities, all of the order of 1 cm^2/V sec, are reasonable for such d-electron materials.[12]

In Fig. 2 we have plotted the thermoelectric power S using the *same* values of the parameters U_0 and α as were used for each of the conductivity fits. The shape of the thermopower curve reflects the gradual shift from conduction by a small number of holes to conduction by a large, fixed number of electrons. Thus, the model explains the small, negative, temperature-independent thermopower observed at high temperatures for $0.01 \leq x \leq 0.12$, a behavior which cannot be understood by one-electron band theory. The magnitude of the high-temperature thermopower is determined primarily by the entropy term,

$-k\alpha'/e$. The values obtained for α' are very close to 0.2, previously suggested by Austin and Mott.[13] The model also successfully predicts the x dependence of the thermopower peak heights, peak locations, and crossover points. At very low temperatures, kT eventually becomes comparable to the bandwidth, and the assumptions of our model break down. Since the Fermi energy then lies within the valence band, the thermoelectric power will fall to zero linearly as T. This effect is responsible for the peaks evident in the data of Fig. 2.

For nominally pure NiS_2, the carrier concentration at low temperatures is determined by nonstoichiometry and the presence of random impurities. Thus, our model cannot be used to fit the data without a detailed knowledge of the nature and density of these impurities. However, if the free-hole concentration for the $x = 0$ sample shown in the figures is 0.006, our model fits the observations quite well.

In conclusion, we have measured the electrical conductivity and thermoelectric power as functions of temperature and composition for the $Ni_{1-x}Co_xS_2$ system, and have found anomalous behavior, unexplainable by one-electron band theory. We have been able, for $x > 0$, to explain quantitatively this anomalous behavior by a model in which the carriers are small polarons in highly correlated, narrow bands. This is the first time, to our knowledge, that a transition resulting from the collapse of a semiconducting gap has been characterized by the predominance of phonon-assisted hopping conduction on both sides of the transition; this contrasts, for example, with the situation in the vanadium oxides, in which the high-temperature phases are metallic. In addition, the small bandwidths necessary to obtain quantitative agreement between theory and experiment suggest that correlation narrowing in Mott-Hubbard insulators can be very large —a fact which helps explain some of the problems in understanding many other materials (for example, NiO). NiS_2 has been studied intensively for about 10 years without a firm conclusion about whether it is a conventional semiconductor or a Mott-Hubbard insulator; our study of the alloy systems strongly supports the conclusion that the latter is the case.

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[1]H. S. Jarrett, W. H. Cloud, R. J. Bouchard, S. R. Butler, C. G. Frederick, and J. L. Gillson, Phys. Rev. Lett. 21, 617 (1968); T. A. Bither, R. J. Bouchard, W. H. Cloud, P. C. Donohue, and W. J. Siemons, Inorg. Chem. 7, 2208 (1968).

[2]J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969); J. A. Wilson and G. D. Pitt, Philos. Mag. 23, 1297 (1971); J. A. Wilson, Adv. Phys. 21, 143 (1972), and in *Phase Transitions*, edited by L. E. Cross (Pergamon, New York, 1973), p. 101.

[3]S. R. Butler and R. J. Bouchard, J. Cryst. Growth 10, 163 (1971).

[4]C. N. Berglund and R. C. Beairsto, Rev. Sci. Instrum. 38, 66 (1967); P. C. Eklund and A. K. Mabatah, Rev. Sci. Instrum. 48, 775 (1977).

[5]R. L. Kautz, M. S. Dresselhaus, D. Adler, and A. Linz, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972*, edited by the Polish Academy of Sciences (PWN —Polish Scientific Publishers, Warsaw, 1972), p. 807.

[6]S. Ogawa, S. Waki, and T. Teranishi, Int. J. Magn. 5, 349 (1974).

[7]J. Hubbard, Proc. Roy. Soc. London, Ser. A 276, 238 (1963).

[8]R. A. Bari, Phys. Rev. B 10, 1560 (1974).

[9]E. J. Yoffa and D. Adler, Phys. Rev. B 12, 2260 (1975).

[10]G. Beni, Phys. Rev. B 10, 2186 (1974).

[11]R. R. Heikes, in *Thermoelectricity*, edited by R. R. Heikes and W. U. Ure (Interscience, New York, 1961), Chap. IV.

[12]D. Adler, in *Solid State Physics*, edited by Henry Ehrenreich, Frederick Seitz, and David Turnbull (Academic, New York, 1968), Vol. 21.

[13]I. G. Austin and N. F. Mott, Adv. Phys. 18, 41 (1969).