PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 691-694

ELECTRONIC STRUCTURE OF NICKEL DICHALCOGENIDES

P. Kwizera, A.K. Mabatah, D. Adler and M.S. Dresselhaus

Center for Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139, USA

Results for the transport properties of nickel dichalcogenides cannot be understood using the conventional one electron approach. However, a model that invokes both strong electronic correlations and electron-phonon coupling in the 3d-e_g band of Ni^{2+} explains the results quantitatively and implies that NiS_2 is a Mott insulator, with an energy gap arising from correlation splitting of the Ni^{2+} e_g band and transport is predominantly by small polaron hopping.

I. Introduction

The anomalous electrical properties of NiS_2 have received considerable attention recently [1,2]. The usual one electron band model requires that the 3d-e_g band contain four states per cation, so that FeS_2 has an empty e_g band and ZnS_2 has a completely filled e_g band, while CoS_2 and CuS_2 have one-quarter and three-quarter filled e_g-bands, respectively. Thus, ZnS_2 and FeS_2 are insulators and CoS_2 and CuS_2 are metallic. However, this scheme predicts that NiS_2 would have a half-filled e_g band, and thus also be metallic. However, pure stoichiometric NiS_2 is semiconducting. This anomaly makes NiS_2 the most interesting of these materials. It has recently been demonstrated that NiS_2 is a Mott insulator because of the fact that electronic correlations split the e_g band into two sub-bands [1,2].

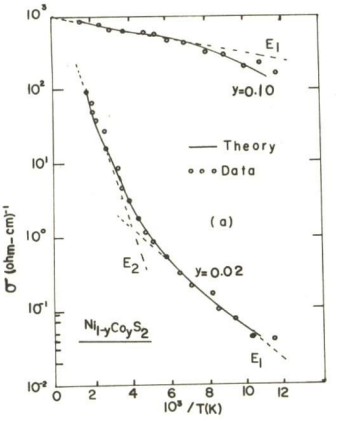
In this paper we report the results of electrical conductivity Hall effect, and thermoelectric power measurements on single crystals of $Ni_{1-y}Co_yS_2$ ($0 \lesssim y \lesssim 0.12$), $NiS_{2-x}Se_x$ ($0 \lesssim x \lesssim 0.6$), and $Ni_{1-z}Cu_zS_2$ ($0 \lesssim z \lesssim 0.07$). The results are interpreted quantitatively in terms of a model in which the effect of both electronic correlations and electron-phonon interaction are important.

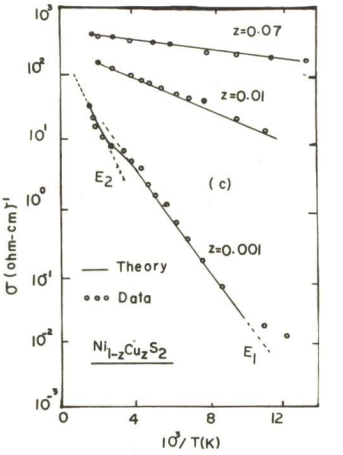
II. Experimental Procedure and Results

The experimental procedures used are described more fully elsewhere [1-4]. Single crystals were grown by chemical vapor transport [3] and characterized by x-ray lattice constant measurements and chemical analysis. The conductivity and Hall effect measurements were made using the Vander Pauw method. Thermopower measurements were made using a heat pulse technique [4].

The main features of the results of the conductivity and thermopower measurements are shown in Figs. 1-2. In the Co system, there are three characteristic regimes, with activation energies E_1 ($\sim$30 meV) and E_2 ($\sim$200 meV) (Fig. 1(a)). E_1 is associated with

hopping activation and E_2 with activation across an energy gap. An interesting feature is the high temperature behavior for $0.05 \lesssim y \lesssim 0.12$ where the activation energy is E_1, and this is associated with hopping after collapse of the energy gap due to screening provided by thermally generated carriers. For the selenium system, the high temperature behavior is similar in the semiconducting regime ($x<0.6$) except that no temperature-induced band collapse is observed. A very interesting feature (Fig. 1(b)) first reported by Bouchard et al. [5] is the quasimetallic phase for $0.4 \lesssim x \lesssim 0.55$, $T<150K$. This cannot be due to a semiconductor-metal transition since polaron conduction predominates in the very same materials at high temperatures [2]. We identify this regime as one in which small polaron band conduction predominates. The results of the conductivity measurements for the $Ni_{1-z}Cu_zS_2$ ($0 \lesssim z \lesssim 0.07$) (Fig. 1(c)), can be similarly characterized by two activation energies E_1 and E_2 again associated with hopping and energy gap activation respectively. For $z \gtrsim 0.005$, where $U_0 \simeq 0$ corresponding to the disappearance of the correlation splitting, hopping type conduction persists also as in the Co system where hopping conduction persists after temperature induced band collapse.





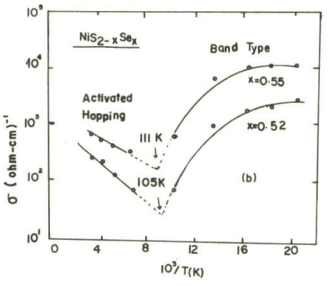


Fig. 1 Conductivity versus inverse temperature showing activated behavior (1(a), 1(c)); 1(b) shows polaron-band conduction

The results for the thermopower measurements are very similar in all the systems in the semiconducting regimes.

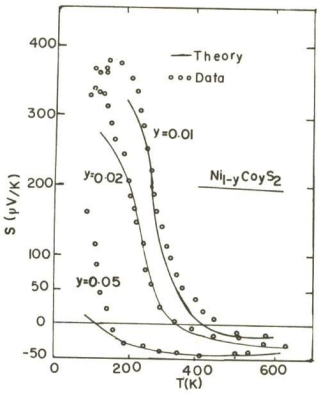


Fig. 2 Thermopower versus temperature for $Ni_{1-y}Co_yS_2$: This behavior is typical for the semiconducting regime

Fig. 2 shows the typical behavior with temperature and concentration for the Co system. For the other two systems the behavior of S with x,z and T are very similar to that in the Co system (Fig. 2) except that in the Cu system no temperature-independent region is seen, nor does the thermopower change sign for $0 \lesssim z \lesssim 0.07$, $4K \lesssim T \lesssim 600K$.

Hall effect combined with σ measurements could be used to separate the effects of variation of concentration of carriers from effects of their mobility. Unfortunately, for all our samples, the Hall voltage, V_H, was too small to detect ($V_H < 2\ \mu V$ for $100 \lesssim T \lesssim 300K$, $0 \lesssim B \lesssim 150kG$). We obtain an upper limit of 0.5 $cm^2/Vsec$ for the Hall mobility in this regime.

III. Discussion

A. Model for Transport Properties of Nickel Dichalcogenides

Our results for the $Ni_{1-y}Co_yS_2$ and $NiS_{2-x}Se_x$ systems can be interpreted in terms of a model in which strong electron correlations in the narrow $3d\text{-}e_g$ band splits the e_g band into two narrow sub-bands [1,2]. The energy gap for the narrow bands is given by $Eg=U$, where U is the intraionic Coulomb energy. In pure stochiometric NiS_2 the lower band is full and the upper one empty at T=0. If small polarons form [6], the bandwidth is much smaller than U and $Eg \simeq U$. Screening effects due to thermally excited carriers result in a decrease in U, $U=U_o-CT$, U_o and C are constants. The conductivity and thermopower S, in this approximation have been calculated to give analytic expressions for σ, and S [1,2,7]. The expressions for σ and S contain parameters which can be obtained from the data [1,2]. For example, in Fig. 1(a) $\sigma = n(T)\mu e \propto \exp\{-\beta(E_H + 1/2\ U_o)\} \propto \exp -\{\beta(E_1 + E_2)\}$. Thus at low temperatures the slope of $\ln \sigma$ versus $1/T$ is $E_1=E_H$ which is the hopping energy both below and above the temperature where the band gap vanishes. The intermediate regime is characterized by a slope $E_H + 1/2\ U_o$ corresponding to E_1+E_2. With this type of procedure we have fit the

data for σ and S as shown in Figs. (1) and Fig. (2).

B. Polaron-Band Conduction in $NiS_{2-x}Se_x$ $0.4 \lesssim x \lesssim 0.55$

For this regime, the samples appear to undergo a transition to a metallic state at low temperatures (see Fig. 1(b)). Holstein [6] has shown that a polaron band should form at low temperatures, and that as the temperature is increased we should expect a region of exponentially decreasing conductivity followed by a region of exponentially increasing conductivity. Lang and Firsov [8] further predicted that the transition temperature between the two regimes increases with increasing bandwidth. Fig. 1(b) shows that predicted behavior, and we consequently conclude that transport at temperatures below the cusp is due to polaron-band formation.

IV. Conclusions

We have presented experimental results for the conductivity, thermoelectric power, and Hall effect, as a function of temperature for single crystals of the $NiS_{2-x}Se_x$, $Ni_{1-y}Co_yS_2$, and the $Ni_{1-z}Cu_zS_2$ systems. All the results in the three alloy systems are consistent with the conclusion that NiS_2 is a Mott insulator, as a result of electron correlation splitting of the Ni^{2+} $3d e_g$ band. In all systems, Ni vacancies and/or trace impurities lead to small hole concentrations [9]. Cobalt doping increases the number of holes, but polaron transport remains the predominant conduction mechanism even after the temperature-induced collapse of the band gap [1]. Selenium doping increases the bandwidth without changing the carrier density and the behavior is as predicted by the model [2]. For $0.4 \lesssim x \lesssim 0.55$, $T < 150K$, the $NiS_{2-x}Se_x$ exhibits the formation of small polaron bands, as predicted by Holstein [6]. For the $Ni_{1-z}Cu_zS_2$ system, the behavior of the conductivity is also just as predicted by the model. However, the thermopower has a different sign from that expected, most likely due to a much higher mobility for holes than for electrons.

Acknowledgment

This research was supported by the U.S. National Science Foundation Materials Research Laboratory Grant #DMR-78-24185.

References

1) A.K. Mabatah, Ellen Yoffa, P.C. Eklund, M.S. Dresselhaus and D. Adler: Phys. Rev. B21 (1980) 1676.
2) P. Kwizera, M.S. Dresselhaus and D. Adler: Phys. Rev. B21 (1980) 2328.
3) R.J. Bouchard: Mater. Res. Bull. 3 (1968) 563.
4) P.C. Eklund and A.K. Mabatah: Rev. Sci. Instrum. 48 (1977) 775.
5) R.J. Bouchard, J.L. Gillson and H.S. Jarret: Mat. Res. Bull. 9 (1973) 489.
6) T. Holstein, Ann. Phys. (N.Y.) 8 (1959) 325.
7) E.J. Yoffa and D. Adler: Phys. Rev. B12 (1976) 2260.
8) I.G. Lang and A. Yu. Firsov: Fiz. Tver. Tela (Leningrad) 5 (1963) 2799. [Sov. Phy. Solid State 5 (1964) 2049].
9) G.K. Krill, M.E. Lapierre, F. Gautier, C. Robert, G. Czjzek, J. Fink and H. Schmidt: J. Phys. C. 9 (1976) 761.