PHYSICAL REVIEW B VOLUME 58, NUMBER 15 15 OCTOBER 1998-I

Photoemission study of the metal-insulator transition in $NiS_{2-x}Se_x$

K. Mamiya,* T. Mizokawa, and A. Fujimori
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

T. Miyadai
Faculty of Fine Arts, Dohto University, Kita-Hiroshima 061-11, Japan

N. Chandrasekharan, S. R. Krishnakumar, and D. D. Sarma
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

H. Takahashi
College of Humanities and Sciences, Nihon University, Setagaya-ku, Tokyo 156, Japan

N. Môri
Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan

S. Suga
Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka 560, Japan

(Received 6 April 1998)

We have studied the electronic structure of $NiS_{2-x}Se_x$, which undergoes a metal-insulator transition as functions of composition x and temperature, by means of photoemission and inverse-photoemission spectroscopy. Spectral changes across the transition near the Fermi level (E_F) (particularly within ~100 meV of E_F) have been interpreted as due to a ''semimetallic'' closure of the band gap in going from the insulating phase to the antiferromagnetic metallic phase. On the other hand, there is also composition- and temperature-dependent spectral weight transfer over a wider energy range of ~0.5–1 eV, indicating significant correlation effects. Photoemission intensity just below E_F remains high in the insulating phases, indicating that the carrier number is large at high temperatures and that the activation-type transport is due to the activated mobility rather than the activated carrier number. [S0163-1829(98)07536-5]

I. INTRODUCTION

Metal-insulator transitions caused by strong electron correlation have been the subject of extensive research for a long time.[1] Many studies have been done for such systems as V_2O_3, Ti_2O_3, NiS, and $NiS_{2-x}Se_x$, which show metal-insulator transitions as functions of temperature, pressure, and chemical composition. Pyrite-type $NiS_{2-x}Se_x$ undergoes an insulator-to-metal transition with increasing x.[2–6] Because the metal-insulator transition in this system is not accompanied by a change in the crystal symmetry, it is believed to be driven by electron-electron interaction, i.e, a Mott transition.

The electronic and magnetic-phase diagram of $NiS_{2-x}Se_x$ is shown in Fig. 1.[4] NiS_2 is an antiferromagnetic insulator with $T_N = 40$ K.[2] The activation energy of the electrical conductivity in NiS_2 varies with temperature:[3] it is ~70 meV at room temperature and becomes ~300 meV at higher temperatures. The optical absorption spectra of NiS_2 show a gap of ~300 meV.[3] NiS_2 becomes an antiferromagnetic metal for a ~23% substitution of Se for S, i.e., $NiS_{1.5}Se_{0.5}$.[4] The activation energy decreases as the composition approaches the insulator-metal phase boundary.[5] The Néel temperature T_N increases with x in the insulating phase, then decreases and is suppressed to 0 K for ~50% Se substitution in the metallic phase. There is an interesting composition region near $x = 0.5$, where $NiS_{2-x}Se_x$ undergoes a transition from an antiferromagnetic metal to a semiconductor with increasing temperature. The Hall measurements above ~200 K indicate that the carrier number in the paramagnetic insulating phase ($x \sim 0.5$) is nearly identical to that in the paramagnetic metallic phase ($x > 0.5$).[6] Surprisingly, the carrier number *decreases* in going from the paramagnetic insulating phase to the antiferromagnetic metallic phase in $NiS_{1.5}Se_{0.5}$. The magnetic susceptibility above T_N is Curie-Weiss-like in NiS_2 and Pauli paramagnetic in $NiSe_2$.[7,8]

In this paper, we have performed photoemission and inverse-photoemission experiments at various temperatures and compositions, in order to study how the electronic structure of $NiS_{2-x}Se_x$ on the low-energy scale is responsible for the transport properties and the metal-insulator transitions. So far, photoemission and inverse-photoemission studies of $NiS_{2-x}Se_x$ have been reported by several groups.[9–12] Recently, a cluster-model analysis of the photoemission spectra has been made for NiS_2 and the charge-transfer nature of the band gap has been revealed.[11] An angle-resolved photoemission study (ARPES) of NiS_2 and $NiS_{1.5}Se_{0.5}$ has revealed a strong temperature dependence of the electronic structure near the Fermi level in the latter compound.[12]

II. EXPERIMENT

Single crystals with compositions $x = 0$, 0.66, and 2 were synthesized by the vapor-transport method. Polycrystalline

© 1998 The American Physical Society

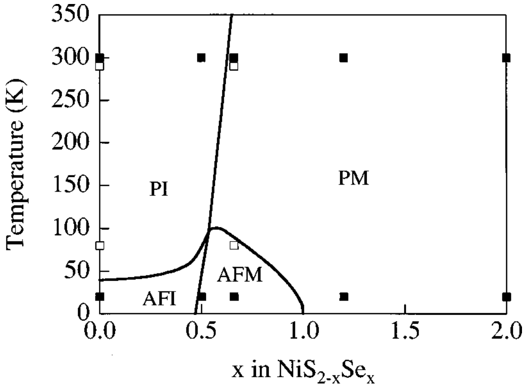


FIG. 1. Phase diagram of $NiS_{2-x}Se_x$ (Refs. 4 and 6). AFI, antiferromagnetic insulator; AFM, antiferromagnetic metal; PM, paramagnetic metal; PI, paramagnetic insulator. Solid squares indicate compositions and temperatures where the high-resolution PES measurements were made in this work. Open squares indicate compositions and temperatures where the conventional-resolution PES and BIS measurements were made.

samples with nominal compositions $x=0.45$ and 1.20 were also studied. The metal-insulator transition temperature of the $x=0.45$ sample was found to be ~60 K. According to the phase diagram (Fig. 1), the $x=0.45$ sample should have an actual composition of $x\simeq 0.50$. Therefore, we refer to the nominally $x=0.45$ sample as $x=0.5$ hereafter. Uncertainties in the chemical compositions of similar extent might be present in the other samples but would not alter the conclusions of this paper.

Photoemission spectroscopy (PES) and bremsstrahlung isochromat spectroscopy (BIS) measurements with conventional energy resolution for $x=0$ and 0.66 were performed at liquid nitrogen temperature. The total instrumental resolution of PES and BIS was 0.3 and 0.9 eV, respectively. High-resolution PES measurements for $x=0$, 0.5, 0.66, 1.2, and 2 were performed at 300 and 15 K with a total energy resolution of ~25 meV. The light source used for the PES measurements was the resonance lines of He I (21.2 eV) and He II (40.8 eV). The photoionization cross section of Ni 3*d* orbitals is dominant for incident photons of 40.8 eV, while those of Ni 3*d*, S 3*p*, and Se 4*p* are comparable for incident photons of 21.2 eV. In order to obtain clean surfaces, the samples were repeatedly scraped *in situ* with a diamond file.

III. RESULTS

Figure 2 shows combined PES and BIS spectra of the insulating NiS_2 and metallic $NiS_{1.34}Se_{0.66}$. We have assigned the peak at -1.6 eV to Ni 3*d*-derived states ($d^8\underline{L}$ final states). The double peaks at 1.0 and 2.5 eV are assigned to hybridized states of the S 3*p* (or Se 4*p*) antibonding σ^* states and Ni 3*d* states and the plateau above 6.0 eV to the Ni 4*sp* states. It can be seen that the S 3*p*/Se 4*p* σ^* band and the Ni 3*d* band in the BIS spectrum of $NiS_{1.34}Se_{0.66}$ are shifted toward lower energies by ~0.3 eV compared to those of NiS_2 while the main peak in the PES spectra is not shifted appreciably, leading to a closing of the band gap. The main PES peak of $NiS_{1.34}Se_{0.66}$ is somewhat narrower than that in NiS_2 probably because the multiplet structures in the insulating NiS_2 would be smeared out in the metallic $NiS_{1.34}Se_{0.66}$.

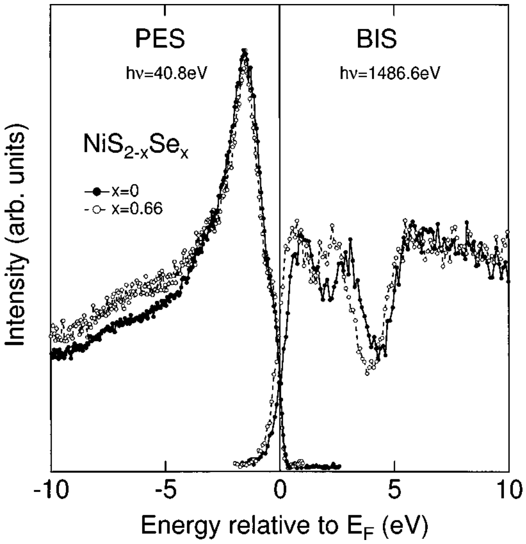


FIG. 2. PES and BIS spectra of NiS_2 (insulator) and $NiS_{1.34}Se_{0.66}$ (metal).

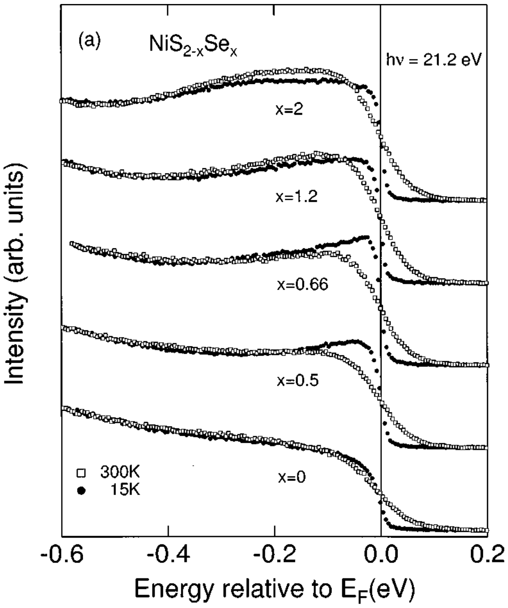
PES spectra near the Fermi level (E_F) for $x=0$, 0.5, 0.66, 1.2, and 2 taken at 15 and 300 K are shown in Figs. 3(a) and 4. Here, the spectra have been normalized below ~ -0.6 eV, where no temperature dependence was observed in the spectral line shapes. The existence of a peak at E_F or slightly below it in the antiferromagnetic metallic phase ($x=0.5$ and 0.66 at 15 K) is different from the metallic NiS, whose spectra show only a flat density of states (DOS) around E_F.[13] In $NiS_{2-x}Se_x$, too, the peak is suppressed in the paramagnetic metallic phase ($x=1.2$ and 2).

Although the optical gap of NiS_2 has been reported as large as 300 meV,[3] the PES spectra do not show such a large gap. In particular, the spectrum taken at 300 K looks like that of a metal with a thermally broadened Fermi edge. The spectrum of $NiS_{1.5}Se_{0.5}$ taken at 300 K (paramagnetic insulator) again looks like a metallic one.

In order to see whether the difference between the spectra taken at 15 and 300 K is simply due to thermal broadening or there are additional changes in the spectra, we have broadened the spectra taken at 15 K with a Gaussian of width $\sim 3.8k_BT$ ($T=300$ K) and plotted with the high-temperature spectra in Fig. 3(b). As for $x=0.5$ and 0.66, one can see that spectral weight is transferred from the region $-(0.2-0.5)$ eV to near E_F in going from the high-temperature paramagnetic phase to the low-temperature antiferromagnetic metallic phase. On the contrary, for the $x=1.2$ and 2 samples, which are paramagnetic metals at all temperatures, spectral weight from E_F to -0.4 eV decreases with decreasing temperature. For NiS_2, too, the spectral weight near E_F slightly decreases with decreasing temperature.

IV. DISCUSSION

There are several implications of the present experimental results for the transport properties and the metal-insulator transition in the $NiS_{2-x}Se_x$ system. As for NiS_2 below T_N, the gap is not observed in the PES spectra probably because the Fermi level is located near the top of the valence band since it shows *p*-type conduction. The spectra of NiS_2 above



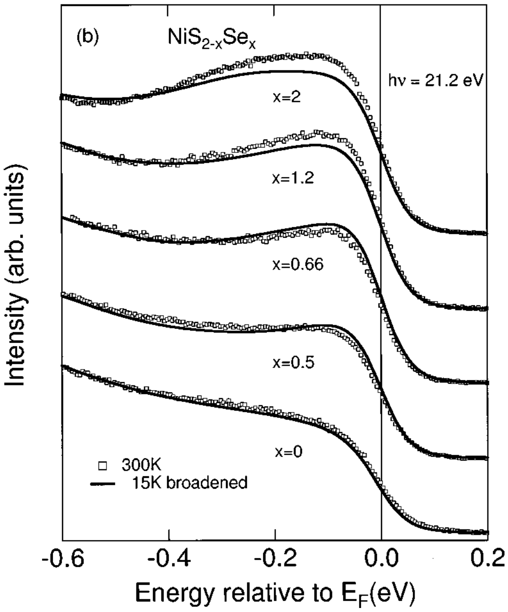


FIG. 3. (a) High-resolution PES spectra of $NiS_{2-x}Se_x$ near E_F. (b) The same as (a) but the spectra taken at 15 K have been artificially broadened to simulate the thermal broadening.

T_N also do not show any visible gap in spite of the gap as large as 300 meV found by the optical absorption study[3] and the ~70 meV activation energy found from the transport study above 170 K.[3,14] The absence of the gap in the PES spectra and hence the proximity of the Fermi level to the top of the valence band implies that the activation energy for the hole carrier number at room temperature is negligibly small and that a large number of hole carriers are thermally activated. Therefore, in order to explain the activation-type transport, the mobility should be activation type and have an activation energy as large as ~70 meV. Indeed, the small mobility $<0.5\ \mathrm{cm^2/Vs}$ deduced from the Hall coefficient measurement is consistent with small polaron hopping, which should show an activated mobility.[14]

The PES spectra for $x=0.5$ in the antiferromagnetic metallic phase, where the carrier concentration is *smaller* than the insulating phase,[6] show an enhanced intensity within 100 meV of E_F compared to the paramagnetic insulating or metallic phase. This increase in the DOS around E_F may be explained by a semimetallic overlap of the conduction and valence bands. The composition-dependent shifts of the PES and BIS spectra (Fig. 2) are consistent with this picture. Indeed, the optical gap of NiS_2 seems to be an indirect one,[3] i.e., the bottom of the conduction band and the top of the valence band seem to be located at different $\vec{k}$ points in the Brillouin zone. The angle-resolved photoemission study of $NiS_{1.5}Se_{0.5}$ by Matsuura *et al.*[12] has indicated a sharp peak just below E_F at a certain $\vec{k}$ point in the Brillouin zone and the peak intensity grows as the temperature decreases from the insulating phase to the metallic phase. On the other hand, we have found that the angle-integrated spectra for $NiS_{1.5}Se_{0.5}$ show less dramatic changes in the line shape and that the total spectral weight integrated from E_F to -600 meV is conserved. Then, the growth of the peak in the angle-resolved PES spectra means that spectral weight is transferred between different $\vec{k}$ points. The ''semimetallic'' closure of the band gap gives a natural explanation to the spectral weight transfer between different $\vec{k}$'s with varying temperature.

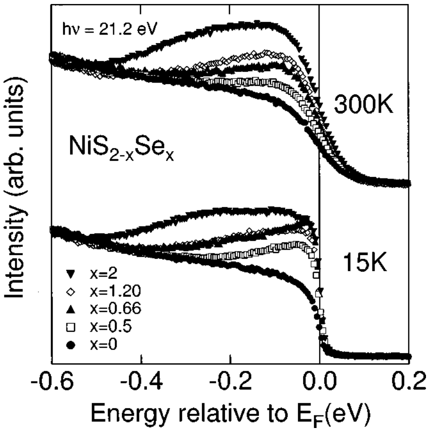


FIG. 4. Composition dependence of the high-resolution PES spectra of $NiS_{2-x}Se_x$ at 300 and 15 K.

The semimetallic picture is also consistent with the recent transport study of $NiS_{2-x}Se_x$ by Miyasaka *et al.*[6] They have found a decrease of the carrier concentration when the metal-insulator boundary $x \simeq 0.5$ is approached from the metallic side. Such a simple semimetallic picture is able to explain the transition between the antiferromagnetic insulating and metallic phases since the band structure does not change drastically between the two phases. On the other hand, the situation becomes more complicated with the strong correlation inherent in the d-electron system, especially in the vicinity of the phase boundary. For example, it is not clear whether the increasing intensity around E_F with x (Fig. 4) can be interpreted solely by the semimetallic overlap of the valence and conduction bands or is dominated by spectral weight transfer from high to low energies with decreased electron-correlation strength.[15] Indeed, Matsuura *et al.*[12] have interpreted their temperature-dependent ARPES data for $x=0.5$ on the basis of the latter scenario. Such spectral-weight transfer has also been observed in a recent BIS study of $NiS_{2-x}Se_x$.[16]

V. CONCLUSION

We have studied the electronic structure of the pyrite-type NiS_2 and its Se-substituted compounds by PES and BIS experiments. High-resolution PES spectra of insulating samples show a high intensity at E_F, particularly at high temperatures. This indicates that a large number of holes are thermally activated at high temperatures but cannot conduct efficiently due to their small mobility. Spectral weight near E_F is enhanced as the Se content is increased. In order to explain the change in the PES spectra across the metal-insulator transition, especially within ~100 meV of E_F, we suggest a ''semimetallic'' overlap of the valence and conduction bands in going from the insulating phase to the antiferromagnetic metallic phase. On the other hand, the composition- and temperature-dependent spectral weight transfer occurs over a wider energy range of 0.5–1 eV, signaling strong correlation effects.

ACKNOWLEDGMENTS

We are grateful to Professor N. Hamada for informative discussions. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture and the Board of Research on Nuclear Science and Department of Science and Technology, Government of India.

---

*Present address: Institute for Material Structure Science, High Energy Accelerator Research Organization, Oho, Tsukuba, Ibaraki 305, Japan.

[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990).

[2] T. Miyadai, K. Takizawa, H. Nagata, H. Ito, S. Miyahara, and K. Hirakawa, J. Phys. Soc. Jpn. **38**, 115 (1975).

[3] R. L. Kautz, M. S. Dresselhaus, D. Adler, and A. Linz, Phys. Rev. B **6**, 2078 (1972).

[4] G. Czjzek, J. Fink, H. Schmidt, G. Krill, M. F. Lapierre, P. Panissod, F. Gautier, and C. Robert, J. Magn. Magn. Mater. **3**, 58 (1976).

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

[6] S. Miyasaka, H. Takagi, Y. Sekine, H. Takahashi, N. Môri, and R. J. Cava (unpublished).

[7] S. Ogawa, J. Appl. Phys. **50**, 2308 (1979).

[8] S. Sudo and T. Miyadai, J. Phys. Soc. Jpn. **54**, 3934 (1985).

[9] G. Krill and A. Amamou, J. Phys. Chem. Solids **41**, 531 (1980).

[10] W. Folkerts, G. A. Sawatzky, C. Haas, R. A. de Groot, and F. U. Hillebrecht, J. Phys. C **20**, 4135 (1987).

[11] A. Fujimori, K. Mamiya, T. Mizokawa, T. Miyadai, T. Sekiguchi, T. Takahashi, N. Môri, and S. Suga, Phys. Rev. B **54**, 16 329 (1996).

[12] A. Y. Matsuura, Z.-X. Shen, D. S. Dessau, C.-H. Park, T. Thio, J. W. Bennett, and O. Jepsen, Phys. Rev. B **53**, R7584 (1996).

[13] M. Nakamura, A. Sekiyama, H. Namatame, H. Kino, A. Fujimori, A. Misu, H. Ikoma, M. Matoba, and S. Anzai, Phys. Rev. Lett. **73**, 2891 (1994); D. D. Sarma, S. R. Krishnakumar, N. Chandrasekharan, E. Weschke, C. Schüssler-Langeheine, and G. Kaindl, *ibid.* **80**, 1284 (1998).

[14] A. K. Mabatah, E. J. Yoffa, P. C. Eklund, M. S. Dresselhaus, and D. Adler, Phys. Rev. B **21**, 1676 (1980).

[15] A. Fujimori, I. Hase, H. Namatame, Y. Fujishima, Y. Tokura, H. Eisaki, S. Uchida, K. Takegahara, and F. M. F. de Groot, Phys. Rev. Lett. **69**, 1796 (1992).

[16] D. D. Sarma, M. Pedio, M. Capozi, A. Girycki, N. Chandrasekharan, N. Shanthi, S. R. Krishnakumar, C. Ottaviani, C. Quaresima, and P. Perfett, Phys. Rev. B **57**, 6984 (1998).