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OPTICAL REFLECTIVITY SPECTRA AND ELECTRONIC STRUCTURES IN Fe_7Se_8 AND Co_7Se_8

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Abstract. – Spectra of optical conductivity and UPS have been measured in single crystals of Fe_7Se_8 and Co_7Se_8. Experimental spectra in Fe_7Se_8 showed good correspondence with the DOS (density of state) spectrum obtained from the band calculation in FeSe. Magnetic properties of these crystals are discussed in connection with the electronic structures.

1. Introduction

Fe_7Se_8 and Co_7Se_8 crystallize in a NiAs-like structure with a superstructure (3c or 4c) due to ordering of vacant cation sites [1]. The electrical conduction of both materials are metallic, whereas the magnetic properties are different; Fe_7Se_8 is a ferrimagnet and $CoSe_8$ a Pauli-paramagnet [2]. Several anomalous magnetic behaviors have been observed in the solid solution system between the two selenides [3].

We have been studying on the optical properties of these materials to elucidate the relation between the magnetic properties and the electronic structures [4, 5]. In the course of the work we noticed a difference in color between two crystals; i.e. the former is colorless whereas the latter is slightly golden. We, therefore, measured optical reflectivity spectra in these crystals. In addition, we measured ultraviolet photoelectron spectra in Fe_7Se_8 to get insight into the valence band structure of this crystal. These experimental results are discussed in terms of the energy band structure of NiAs type FeSe calculated recently by Morifuji and Motizuki [6].

2. Experimentals

Single crystals of Fe_7Se_8 and Co_7Se_8 were grown from the melt by the Bridgmann technique. Samples for the reflectivity measurements were cut from the ingot and were mirror-polished with lapping films. The surface was slightly etched by using nitric acid solution prior to the ultraviolet measurements.

Reflectivity spectra for photon energies between 0.2 and 4 eV were measured by using specially designed reflectivity spectrometer as used in the previous works on pyrites [7]. Vacuum ultraviolet reflectivity spectra between 3 and 25 eV were measured by using a synchrotron radiation (BL-3) from the storage ring at the Synchrotron Laboratory of ISSP. Reflectivity spectra for 0.2-4 eV and those for 3-25 eV were connected and calibrated by using the absolute values obtained from the ellipsometry at 546 nm. The Kramers-Kronig analyses have been performed by using an ACOS-1000 computer in Tokyo University of Agriculture and Technology.

The ultraviolet photoelectron spectrum was measured by using BL-1 at the Synchrotron Laboratory. The samples was cleaved in the vaccuum. The excitation photon energy region was between 32 and 120 eV, and EDC was measured for binding energies between +0.5 and −20 eV.

3. Results

Figure 1 shows reflectivity spectra in single crystals of Fe_7Se_8 (solid curve) and Co_7Se_8 (dotted curve). The gross features of the two spectra are very close especially for photon energies higher than 8 eV. However, clear distinction can be observed in the energy region lower than 5 eV.

The Kramers-Kronig analyses performed with an extrapolation by the Drude term for lower energies and by E^{-p} dependence on photon energy E for higher energies. Details of the results have been published elsewhere [5]. In figure 2 are shown spectra of the real part of the conductivity (corresponding to the absorption spectra) obtained by the analyses for photon energies lower than 5 eV, in which a clear difference in the spectral features between Fe_7Se_8 and Co_7Se_8 is observed; Fe_7Se_8 shows a sharp and intense absorption peak at 0.5 eV, while Co_7Se_8 a broad and less intense absorption band ranging between 0.5 and 3 eV. This difference in the absorption spectrum can account for the difference in the color of these crystals.

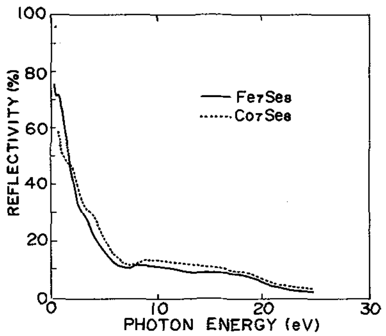

Fig. 1. – Reflectivity spectrum of Fe_7Se_8 (solid curve) and Co_7Se_8 (dotted curve) between 0.2 and 25 eV measured at room temperature.

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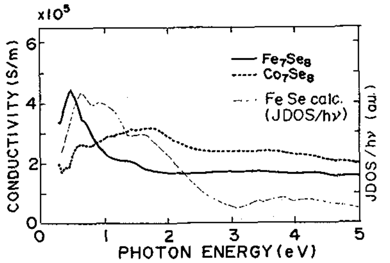

Fig. 2. – Spectra of the real part of conductivity in Fe$_7$Se$_8$ (solid curve) and Co$_7$Se$_8$ between 0.2 and 5 eV. Dashed curve represents a joint density of state of NiAs-type FeSe evaluated from the calculated band structure [6].

Figure 3 shows ultraviolet photoelectron spectra in Fe$_7$Se$_8$ for binding energies between +0.5 and −18 eV. Curves are plotted for several excitation energies between 32 and 120 eV. The cross section for photoelectron emission has been known to be strongly dependent on photoexcitation energy [8]: the cross section of d-electron emission is smaller than that of p-electron for low excitation energies, while the former becomes larger for high energies. The two sharp structures just below the Fermi level appear only for excitations by high photon energies and does not change the position with the excitation energy. They may be assigned to originate from narrow d-bands. On the other hand a broad peak around −6 eV observed in the low excitation energy seems to shift to smaller binding energies as the excitation energy increases and may be correlated with valence band.

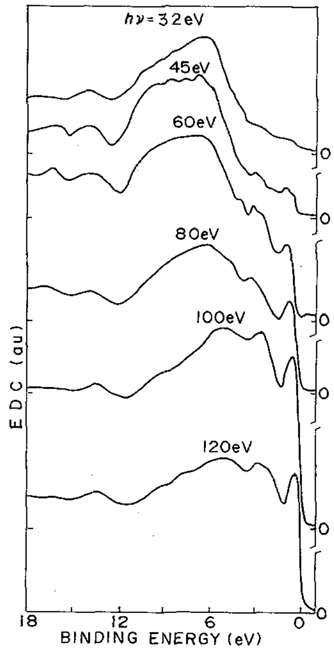

Fig. 3. – Ultraviolet photoelectron spectra of Fe$_7$Se$_8$ for bindidng energies between +0.5 and −18 eV excited by synchrotron radiation.

4. Discussions

Recently an APW band calculation was carried out in FeSe with a NiAs structure by Morifuji and Motizuki [6]. The calculated DOS (density of states) curve below the Fermi level was quite similar to the ultraviolet photoelectron spectrum. They also calculated a JDOS (joint density of states) spectrum from the band structure. The absorption spectrum estimated by deviding JDOS by photon energy is shown by a dashed curve in figure 2. Striking resemblance is seen between the calculated and experimental spectra in spite of the presence of vacant Fe-site in the crystal investigated experimentally.

From these considerations the absorption structure around 0.5 eV in Fe$_7$Se$_8$ can be related to a transition from the d-band below the Fermi level to the d-band above the Fermi level. Therefore, the broad absorption seen at 0.5-3 eV in Co$_7$Se$_8$ can also be associated with a broad d-band width in this material.

We showed in a previous paper on optical studies in a pyrite type solid-solution system, $\mathrm{Co}(\mathrm{S}_{1-x}\mathrm{Se}_x)_2$, that the magnetic properties of the compound are closely related to the width of d-band in the vicinity of the Fermi level [9]. The present optical study also leads to the same conclusion that the compound with a wide d-band near Fermi energy loses a magnetic order to become a Pauli-paramagnet while that with a narrow d-band gains ferrimagnetic order. This conclusion is consistent with the theoretical consideration given by Takahashi and Tano [10].

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[1] Okazaki, A., *J. Phys. Soc. Jpn* **16** (1961) 1162.
[2] Bohm, F., Gronvold, F., Haraldsen, H. and Prydz, H., *Acta Chem. Scand.* **9** (1955) 1510.
[3] Sato, M., Kamimura, T. and Iwata, T., *J. Appl. Phys.* **57** (1985) 3244.
[4] Sato, K., Kida, H. and Kamimura, T., Proc. Int. Symp. Magneto-optics, *J. Magn. Soc. Jpn Suppl.* **11** (1987) 113.
[5] Kida, H., Sato, K., Aman, Y., Kamimura, T. and Fujisawa, M., *J. Magn. Soc. Jpn* **12** (1988) 273 (in Japanese).
[6] Morifuji, M. and Motizuki, K., to be published.
[7] Sato, K., *J. Phys. Soc. Jpn* **53** (1984) 1617.
[8] Yeh, J. J. and Lindau, I., *At. Data and Nucl. Data Tables* **32** (1985) 1.
[9] Sato, K., Sekiguchi, T. and Miyadai, T., *J. Magn. Magn. Mater.* **54-57** (1986) 1033.
[10] Takahashi, Y. and Tano, M., *J. Phys. Soc. Jpn* **51** (1971) 24, 1972.