

REFLECTIVITY AND MAGNETO-OPTICAL SPECTRA IN A SINGLE CRYSTAL OF Fe_7Se_8

K. SATO, H. KIDA, and T. KAMIMURA*

Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

**Tohoku University, Sendai, Miyagi 980, Japan*

ABSTRACT

Optical and magneto-optical properties of a single crystal of metallic ferrimagnet Fe_7Se_8 grown by Bridgmann technique have been measured. This material crystallizes in hexagonal NiAs structure with a superstructure associated with the ordering of vacant Fe sites. Spectra of normal incidence reflectivity and polar magneto-optical Kerr effect were measured at room temperature. From these spectra diagonal and off-diagonal elements of conductivity tensor were evaluated. The results do not clearly show a contribution of intraband transition to the magneto-optical effect, but suggest a contribution of a band-to-band transition starting just below 0.5 eV. This implies the existence of a spin-orbit coupled band with large density of states just below the Fermi-level as supposed from its magnetic properties.

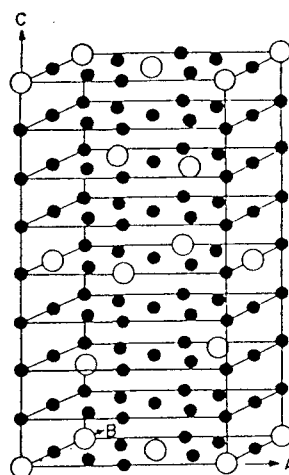
1. INTRODUCTION

There are growing interests in transition metal compounds with NiAs type crystal structure as they have become interpreted in terms of itinerant electron magnetism. For example, recent energy band calculation on MnAs with NiAs structure suggests the appearance of a narrow d-band with high density of states in the vicinity of Fermi surface, which explains the ferromagnetism in this material.[1] It is, therefore, required to get information of electronic structures from experiments. As has been proved in the studies of a series of pyrite type compounds[2], optical and magneto-optical investigations provide powerful and helpful information for discussion of the relation between magnetism and electronic structures.

In this study we take up a ferrimagnetic selenide Fe_7Se_8 with NiAs structure and aim at getting some insight into the electronic structures of this compound through optical measurements. Fe_7Se_8 is one of the small number of chalcogenide crystals which show net magnetic moment at room temperature. It crystallizes in basically a hexagonal NiAs type structure but shows a superstructure with four times the period in c-axis at room temperature, as shown in Fig. 1.[3] Magnetic properties was explained in an ionic model in which divalent iron and vacancy induced trivalent iron couple antiferromagnetically.[4] The easy axis of magnetization exists in the c-plane at room temperature and stands up toward the c-axis when temperature is lowered below 220 K.[5]

Neutron diffraction studies were performed by Kawaminami et al. None of the calculation based on the ionic model, however, could explain the magnetic structure factor of Fe_7Se_8 observed by neutron diffraction study. A metallic ferrimagnet model with Fe moment of $2 \mu_B$ could provide closer value to the experiment.[6] The electrical resistivity shows a curious behavior; a metal-like temperature-dependence is observed below 100 K, above which it takes nearly a constant value $2 \times 10^{-4} \Omega \text{ cm}$ up to 350 K followed by a slight decrease.[7] Moreover, the gamma value of specific heat $\gamma = 8 \text{ mJ/moleK}^2$ was reasonably explained in terms of electrons in a narrow d-band with large density of state.[7] Although these experimental results seem to support the itinerant model no theory has given clear explanation of the magnetic properties in this model.

In this paper we present some results of optical and magneto-optical studies of this material in order to get insight into the electronic band structures.



● Fe site, ○ vacant Fe site
Fig. 1 Crystal structure of Fe_7Se_8 (4c-structure)

2. EXPERIMENTAL

Single crystal of Fe_7Se_8 has been grown from a melt by directional freezing technique. Optical studies were carried out on a polished surface cut from the ingot. The crystal plane of the surface was analyzed by X-ray technique and proved to be nearly (110), which contains c-axis. Nearly normal incidence reflectivity spectra were measured between 0.5 and 3 eV using an apparatus as described elsewhere.[8] Polar Kerr effect spectra were measured by means of polarization modulation technique, the details of which has also been published elsewhere.[9] Since the measured surface contains the c-axis, anisotropic behavior really exists, which causes a phase shift difference between ordinary and extraordinary rays. The phase shift difference spectrum was also measured using the polarization modulation method. All measurements were carried out at room temperature.

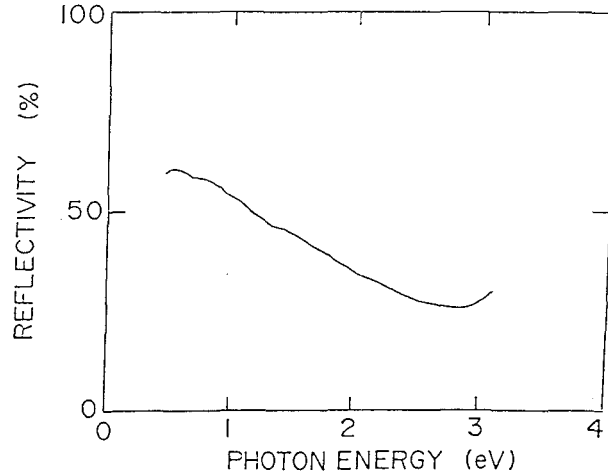


Fig. 2 Reflectivity spectrum of Fe_7Se_8 at nearly normal incidence.

3. RESULTS AND DISCUSSIONS

Fig. 2 illustrates the reflectivity spectrum of Fe_7Se_8 measured with unpolarized light at room temperature. Absolute value of reflectivity was calibrated by using the values of optical constants n (refraction index) and k (extinction coefficient) obtained by ellipsometry with Na lamp. Nearly monotonic decrease of reflectivity with increase of photon energy can be observed in this spectrum. No abrupt increase of reflectivity as seen in CoS_2 , below 0.7 eV could not be observed. Real and imaginary parts of diagonal element of the conductivity tensor was calculated by means of Kramers-Kronig analysis and are shown in Fig. 3. Here we neglected the in-plane anisotropy and assumed xx -component and yy -component are the same. In the Kramers-Kronig analysis we adopted the method introduced by Roessler; parameters were so determined as to realize the values of n and k obtained by ellipsometry.

Generally speaking, conductivity is described in terms of the collective motion of conduction electrons and the band-to-band transitions. The former term is described by so-called Drude formula as follows;

$$\sigma_{xx} = \omega_p^2 / (\omega^2 + 1/\tau^2) \tau + i \omega \omega_p^2 / (\omega^2 + 1/\tau^2) \quad (1)$$

Here $\omega_p^2 = Ne^2/m^*$, where N is the number, e the charge and m^* effective mass of conduction electrons. The former term provides the real part of σ_{xx} that decreases as $1/\omega^2$ and the imaginary part

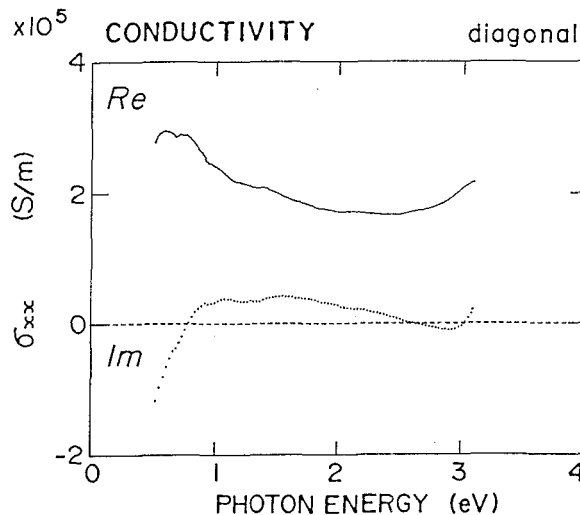


Fig. 3 Real and imaginary parts of diagonal element of conductivity as obtained by Kramers-Kronig analysis of reflectivity.

σ_{xx} that shows $1/\omega$ dependence. These dependence, however, does not apply to the conductivity shown in Fig. 3. Although there remains much uncertainty in the low energy region due to lack of the experimental data below 0.5 eV, the real part of the diagonal conductivity shown in Fig. 3 seems to be originated from a strong band to band transition starting at somewhere below 0.5 eV.

Next, we measured the magneto-optical spectra on this material. No magneto-optical data except for the magnetic birefringence have been reported. Since this crystal is opaque we had to measure magneto-optical spectra by reflection(Kerr effect). Indeed almost no Kerr rotation was observed in the visible region. In the infrared region, however, reflectance magneto-circular dichroism(RMCD) could be observed: A typical hysteresis curve of RMCD at 1 μ m is plotted in Fig. 4. Since magnetic saturation effect is clearly seen in this curve, it is confirmed that the magnetic field is applied parallel to the easy axis of magnetization.

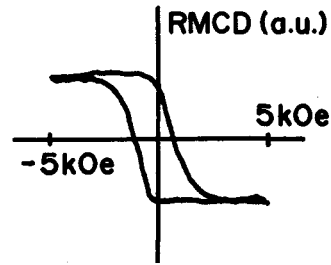


Fig. 4 Hysteresis curve of RMCD

Polar Kerr spectra (rotation and RMCD) are shown in Fig. 5. Well-defined peak of RMCD can be seen around 1.1 eV. Derivative-shaped Kerr rotation spectrum with the center around 1.2 eV is observed. The peak value of Kerr rotation is very small: not more than 2 min. This may be partly due to small net moment of this crystal.

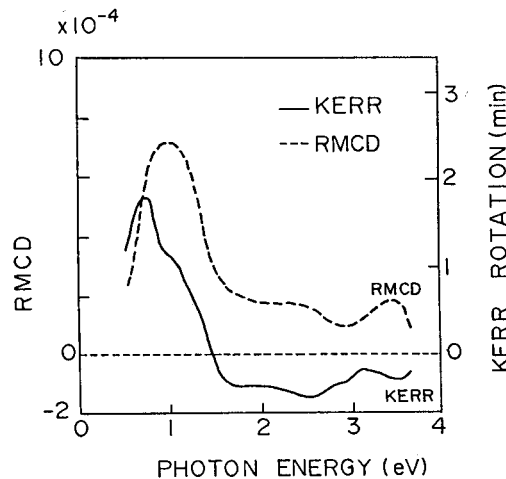


Fig 5 Polar Kerr rotation and RMCD(reflectance magnetocircular dichroism) spectra of Fe_7Se_8 measured at room temperature.

Real and imaginary parts of off-diagonal element of conductivity tensor were evaluated from Kerr rotation ϕ_K and RMCD $\Delta R/R$ using the following formulae with the help of n and k calculated from Kramers-Kronig analysis. Here σ_{xy}' denotes the real part and σ_{xy}'' imaginary part.

$$\begin{aligned} \sigma_{xy}' &= -\epsilon_0 \omega \{k(1-3n^2+k^2) \phi_K - (1/4)n(1-n^2+3k^2) \Delta R/R\} \\ \sigma_{xy}'' &= -\epsilon_0 \omega \{n(1-n^2+3k^2) \phi_K + (1/4)k(1-3n^2+k^2) \Delta R/R\} \end{aligned} \quad (2)$$

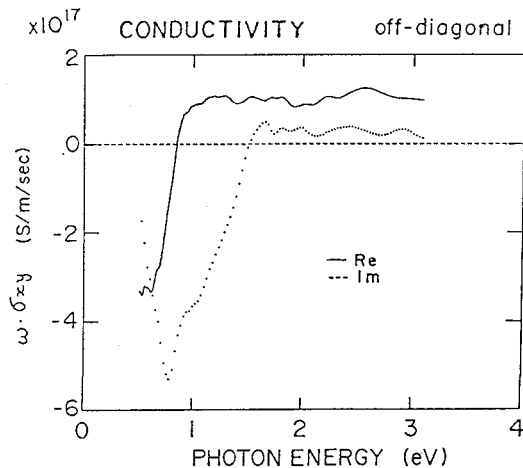


Fig. 6 Real and imaginary parts of off-diagonal element of conductivity tensor between 0.5 and 3 eV.

The diagonal element also has contribution from both intraband and interband transitions. As for the intraband contribution, Erskine and Stern [10] showed that the magneto-optical effect can be described in terms of the "skew scattering" of conduction electrons as follows:

$$\begin{aligned}\sigma_{xy}'(\omega) &= -\epsilon_0 \omega p^2 \langle \sigma_z \rangle (P_0 / e v_0) / \omega^2 \tau^2 \\ \sigma_{xy}''(\omega) &= \epsilon_0 \omega p^2 \langle \sigma_z \rangle (P_0 / e v_0) / \omega \tau\end{aligned}\quad (3)$$

Here $\langle \sigma_z \rangle$ denotes the degree of the spin polarization, P_0 induced dipole moment, v_0 Fermi velocity. Thus the real part has a frequency dependence of $1/\omega^2$, while the imaginary part $1/\omega$. For the ease of comparison, the off-diagonal conductivity elements multiplied by frequency are shown in Fig. 6; if we find such a dependence as $\omega \sigma_{xy}'' = \text{constant}$ the intraband contribution should be important. Almost no such contribution can be observed in that figure. Instead, the imaginary part, which is an "absorptive" component, shows a band with a peak around 1 eV starting at some energy below 0.5 eV. This fact suggests existence of a narrow band below or above Fermi level, which contributes to the magneto-optical transition.

It is well known that in the case of reflection a phase shift between the incident and reflected beam arises on the surface of absorbing material. If we consider a normal incidence reflection by the surface of an optically uniaxial crystal the phase shift becomes different for ordinary and extraordinary rays, i.e. a phase shift difference occurs. The difference is expressed as

$$\Delta \phi = \phi_e - \phi_o \sim 2(k_e - k_o) / (n_{av}^2 - 1) \quad (n_e \sim n_o \sim n_{av}) \quad (4)$$

where suffices o and e mean the ordinary and the extraordinary rays, respectively.[11] We could observe the phase shift difference spectrum as shown in Fig. 7. This figure also suggests the existence of a transition rising at about 0.5 eV.

Since there have been no available energy band calculations in this material, definite assignment of the spectra of conductivity tensor is difficult. The only available energy level scheme is the qualitative model on FeS proposed by White and Mott [12], in which they located both t_{2g} and e_g bands above p band of anion and placed the Fermi level in e_g with up spin and t_{2g} with down spin. If this is also the case in FeSe, we can expect that the t_{2g} level is just below the Fermi level. Our optical data, from which band-to-band edge is estimated to be located around 0.5 eV, are consistent with the assumption.

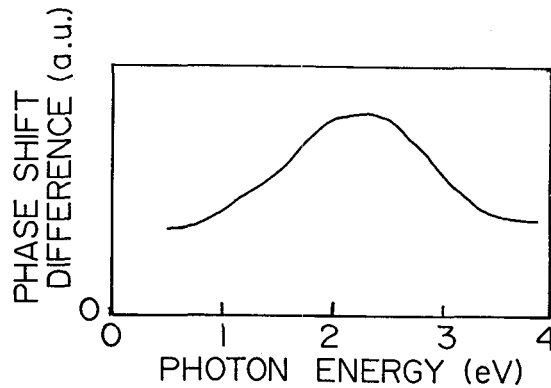


Fig. 7 Phase shift difference spectrum in Fe_7Se_8 .

5. CONCLUSION

We have found through spectroscopic measurements of the reflectivity, the magneto-optical effect and phase shift difference in a single crystal of Fe_7Se_8 , that a strong interband transition starts at the energy below 0.5 eV in this material. Taking into account the fact that in spite of diverse metallic properties the ferrimagnetism of this crystal is explained in terms of ionic model, we can estimate that the narrow d-band is located about 0.5 eV below the Fermi level. This should be ascertained by some kinds of photoemission experiments. Infrared reflectivity measurements at photon energies below 0.5 eV are also necessary to verify the beginning of the band to band transition. In addition, ultraviolet reflectivity spectrum will be helpful to perform more reliable Kramers-Kronig analysis. We are, therefore, planning to carry out these experiments. This work is partly supported by the Grant-in-Aid for Special Project Research from The Ministry of Education, Science and Culture of Japan.

REFERENCES

1. K.Motizuki and K.Kato: J.Phys.Soc.Jpn. 53(1985)735-746.
2. K.Sato: Prog.Cryst.Growth & Char. 11(1985)109-153.
3. A.Okazaki: J.Phys.Soc.Jpn. 16(1961)1162-1170.
4. T.Hirone and S.Chiba: J.Phys.Soc.Jpn. 11(1956)666-670.
5. K.Hirakawa: J.Phys.Soc.Jpn. 12(1957)929-938.
6. M.Kawaminami and A.Okazaki: J.Phys.Soc.Jpn.
7. J.Serre, P.Gibart and J.Bonnerot: J.Phys.(Paris) 30(1969)93-96.
8. K.Sato, M.Morita and F.Sato: Jpn.J.Appl.Phys. 23(1984)1325-1329.
9. K.Sato: Jpn.J.Appl.Phys. 20(1981)2403-2409.
10. J.L.Erskine and E.A.Stern: Phys.Rev. B8(1973)1239-1255.
11. H.Horinaka, N.Yamamoto and T.Miyauchi: Jpn.J.Appl.Phys. 17(1978)521-526.