



**HAL**  
open science

# OPTICAL PROPERTIES OF MAGNETITE (Fe<sub>3</sub>O<sub>4</sub>) IN THE INFRARED

A. Schlegel, P. Wachter

► **To cite this version:**

A. Schlegel, P. Wachter. OPTICAL PROPERTIES OF MAGNETITE (Fe<sub>3</sub>O<sub>4</sub>) IN THE INFRARED. Journal de Physique Colloques, 1980, 41 (C5), pp.C5-19-C5-21. 10.1051/jphyscol:1980504 . jpa-00219939

**HAL Id: jpa-00219939**

**<https://hal.science/jpa-00219939>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

OPTICAL PROPERTIES OF MAGNETITE ( $\text{Fe}_3\text{O}_4$ ) IN THE INFRARED.

A. Schlegel and P. Wachter

*Laboratorium für Festkörperphysik, ETH, 8093 Zürich, Suisse.*

Résumé.- La réflectivité de magnétite ( $\text{Fe}_3\text{O}_4$ ) a été mesurée dans le domaine d'énergie de photon de 0,03 eV jusqu'à 12 eV et analysée en termes des constantes optiques. La variation de la réflectivité avec la température pour les énergies de photon de l'infrarouge reflète la dépendance de la température des transitions "d'intrabande" des électrons de conduction. De plus elle indique la présence des modes couplés de plasmon-phonon dépendant de la température.

Abstract.- The reflectivity of magnetite ( $\text{Fe}_3\text{O}_4$ ) has been measured in the spectral energy range between 0.03 eV and 12 eV and analysed in terms of the optical constants. The variation of the reflectivity with temperature in the infrared photon energy range reflects the temperature dependence of the "intraband" transitions of the conduction electrons. Moreover it points to the presence of temperature dependent coupled plasmon-phonon modes.

1. Introduction.- Magnetite has attracted continuous interest since the discovery of the metal-nonmetal phase transition at 119K by Verwey et al./1/. Various models have been proposed to describe the mechanism of electrical conduction such as small polaron hopping, the Cullen-Callen band model and a model based on electrons localized on iron-pairs. The references in question are listed in /2/. In this paper we are mainly concerned with the effects of the conduction electrons, i.e. their "intraband" transitions, in relation to the optical spectrum.

Reflectivity.- Figure 1 shows the reflectivity spectrum of a natural grown single crystal of magnetite at 300 K and 20 K in the infrared energy range.

The reflectivity in the infrared energy range is strongly changing with temperature. At 300 K the reflectivity basically increases towards lower photon energies. Cooling the sample to e.g. 20 K results in a drop of the reflectivity. This reflectivity decrease is represented in figure 2 for a wave number of  $450 \text{ cm}^{-1}$  of the incident light. It is quite obvious that this temperature dependence of the reflectivity for this spectral energy is connected with the electrical conductivity of magnetite /1,3,4/. Thus the reflectivity increase towards lower photon energies at room temperature

is obviously due to "intraband" transitions of conduction electrons.

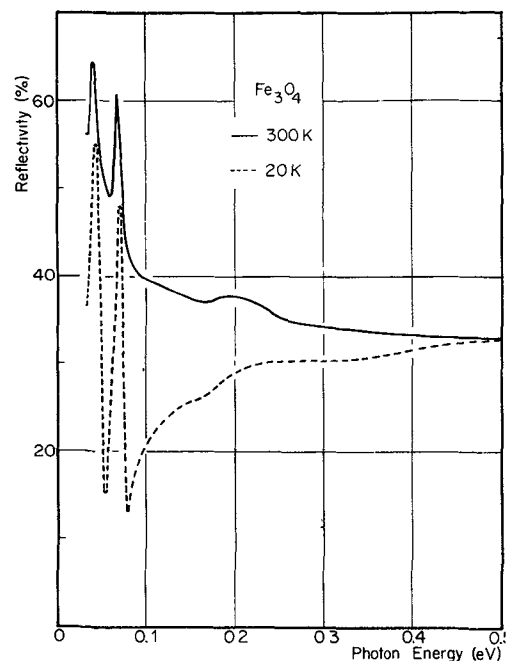


Fig.1 : Reflectivity of magnetite at 300 K (solid line) and at 20 K (broken line).

As this contribution to the spectrum decreases with decreasing temperature, the infrared reflectivity of magnetite below the Verwey transition temperature looks more and more like the one of a semiconductor.

Superimposed in the infrared energy

range one finds at room temperature two sharp reflectivity peaks at 0.042 eV ( $340 \text{ cm}^{-1}$ ) and at 0.068 eV ( $550 \text{ cm}^{-1}$ ) due to infrared active phonons and a relatively weak and broad shoulder at 0.2 eV.

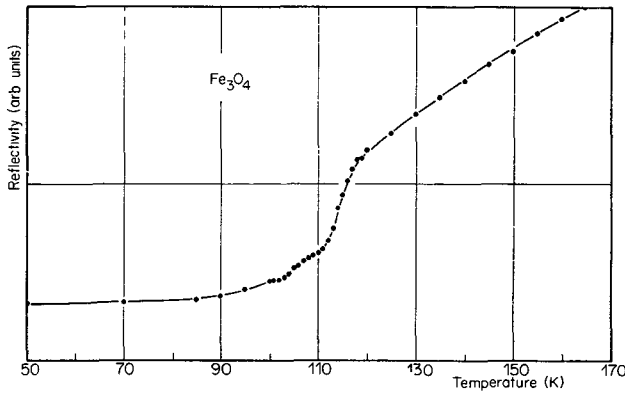


Fig. 2 : Temperature dependence of the reflectivity of magnetite at a photon energy of 0.0558 eV ( $450 \text{ cm}^{-1}$ ) near the Verwey-transition temperature.

Cooling the sample from 300 K to 20 K results in a shift to higher energies by about  $20 \text{ cm}^{-1}$  of the two sharp phonon peaks below 0.1 eV. Simultaneously two sharp reflectivity minima appear on the high energy side of each of the two peaks pointing to the appearance of longitudinal modes. But the reflectivity minimum at 0.06 eV at room temperature is shifted by about  $40 \text{ cm}^{-1}$  to lower energies upon cooling. Under these circumstances one expects coupled plasmon-phonon modes. The uncoupled plasmon frequency increases strongly with temperature which agrees qualitatively with the reflectivity behaviour mentioned above.

2. Optical constants and intraband transitions.

The reflectivity spectrum (actually measured between 0.03 - 12 eV /2/) has been analysed in terms of the optical constants by means of the Kramers-Kronig relation. The reflectivity and the optical constants were checked by an independent polarimetric measurement in the photon range from 0.5 eV up to 5 eV. The extrapolation of the reflectivity below 0.03 eV hardly affects the optical constants above 0.2 eV and only to

an extent of about 10 percent in the range below 0.2 eV. The main source for a systematic error of the optical constants below 0.5 eV are the reflectivity data in this energy range. Figure 3 shows the optical conductivity as it results from the Kramers-Kronig analysis in the infrared energy range for magnetite at 300 K and 20 K.

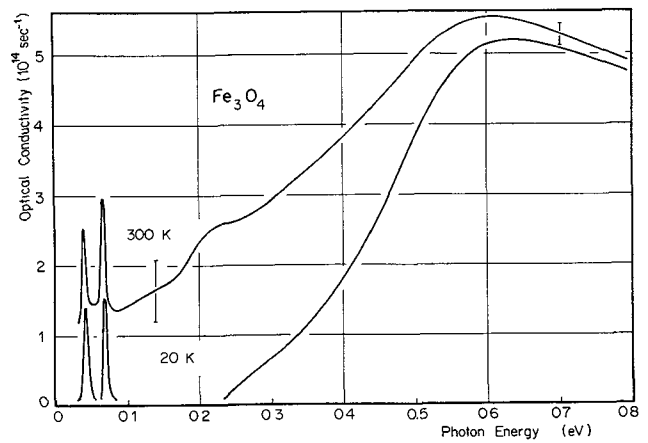


Fig.3 : Optical conductivity of magnetite at 300 K and 20 K from the Kramers-Kronig analysis.

The computed optical conductivity of the sample at 300 K approaches a value between 100 and  $200 \Omega^{-1} \text{ cm}^{-1}$  in the long wave length limit and is in agreement with dc conductivity measurements /4/.

In order to get an idea of the contribution of the conduction electrons, we roughly interpret the difference of the conductivity at 300 K and 20 K as to be due to "intraband transitions". Here we have to neglect the errors introduced by e.g. the shift of the phonon frequencies or the variation in lattice constant due to temperature change. This difference of the optical conductivities should be compared with theoretical models.

Taking tentatively the Drude model, that is

$$\sigma(\omega) = \frac{1}{4\pi} \cdot \frac{\omega_p^2 \cdot \gamma}{\omega^2 + \gamma^2}$$

with  $\omega_p$  being the (unscreened) plasma

frequency and  $\gamma$  the damping, a fit of the data yields the following limits for the parameters  $\omega_p$  and  $\gamma$  :

$$0.5 \text{ eV} < \omega_p < 1.0 \text{ eV}$$

$$0.3 \text{ eV} > \gamma > 1.15 \text{ eV}.$$

The difference of the conductivities in figure 3 follows indeed a Drude behaviour at lower photon energies with deviations near 0.2 eV. The indicated range of the Drude parameters  $\omega_p$  and  $\gamma$  has to be attributed mainly to this deviation. The effective electron concentration, that is  $N^* = \frac{N}{m^*/m_e}$ , using  $N^* = \frac{\omega_p^2}{4\pi e^2}$ , corresponds to a range of  $2 - 7 \times 10^{20} \text{ cm}^{-3}$  or 0.01 - 0.05 per formula unit ( $\text{Fe}_3\text{O}_4$ ), of course assuming the applicability of the Drude model.

Unfortunately, it is yet hardly possible to compare the experimental optical conductivity data with more suitable theoretical models.

Acknowledgment.- The authors are very grateful to Mr. J. Müller for technical assistance.

#### References

- /1/ Verwey, E.J.W. and Haayman, P.W., Physica 8 (1941) 979.
- /2/ Schlegel, A., Alvarado, S.F. and Wachter, P., J. Phys. C. 12 (1979) 1157.
- /3/ Calhoun, B.A., Phys. Rev. 94 (1954) 1577.
- /4/ Samokhvalov, A.A., Tutikov, N.M. and Skornyakov, G.P., Sov. Phys. Solid State 10 (1969) 2172.