Magnetite: Phonon modes and the Verwey transition

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Reflectivity and Raman measurements of magnetite at 300, 130, 80, and 6 K are presented. The four infrared-active phonon modes and the five Raman modes exhibit fine structures below the Verwey transition (120 K), which are clearly detected for what may be the first time. A phenomenological analysis of the phonon spectrum at 130 K is performed.

INTRODUCTION

Magnetite (Fe_3O_4) has been a subject of continuous interest since the discovery of the metal-nonmetal phase transition at 120 K.[1] Several optical investigations of magnetite were carried out, essentially in connection with the, even up to now, unsolved problems of electrical conduction, electronic structure, and Verwey transition.

In addition to spin-polarized photoemission,[2] investigations of the optical and magneto-optical properties of Fe_3O_4 were performed[3,4] in our laboratory over a very large photon energy range. One of the important results of these investigations was the evidence for $3d^n \rightarrow 3d^{n-1}4s$ transitions.

Magnetite is still of actual interest for us, particularly regarding the resolution of the whole phonon spectrum. Waldron,[5] at first, has measured the infrared spectra of seven ferrites in the frequency range 280–4000 cm^{-1}. A cursory inspection of the spectra shows two absorption bands below 1000 cm^{-1} as a common feature of all ferrites. The bands arise from lattice vibrations of the oxide ions against the cations. The theoretical analysis, based on a group-theoretical approach (i.e., factor-group analysis), carried out by White and De Angelis[6] supports Waldron's conclusions. In fact it has been suggested, that a crystal with spinel structure is expected to exhibit four ir-active bands (T_{1u}) and five Raman-active bands (A_{1g}, E_g, and three T_{2g} modes). The four ir active phonon modes correspond to the Fe-O stretching mode of the tetrahedral and octahedral sites, to the Fe-O stretching mode of octahedral sites, where displacements of Fe^{3+} ions of tetrahedral sites are negligible, to the O-Fe-O bending mode of the tetrahedral and octahedral sites and finally to the mode of the motion of ions of the tetrahedral sites against those of octahedral sites, where the displacements of oxygen ions are negligible (see figures in Refs. 5 and 7).

In spite of this, from an experimental point of view, nobody was able, even up to now, to clearly detect the four predicted ir phonons in magnetite; only the two modes at high energy (below 0.1 eV) are unambiguously shown (at 0.042 and 0.068 eV).[3,7–9]

Even though group theory says nothing about the intensities of the bands, we can expect that the last two phonon modes may be weak and it is then necessary to develop high-resolution, low-temperature far-infrared (FIR) measurements.

EXPERIMENT

We have used best quality natural single crystals, polished and annealed for 24 h at 720 °C. We have also performed measurements on synthetic single crystals, supplied by Dr. V. A. M. Brabers (University of Technology, Eindhoven), that present in $R(\omega)$, besides the same features of the natural crystals, many oscillations in the frequency range between 10 and 200 cm^{-1}. This is a subject of present investigations, that will be divulged in a further publication. For clarity we present here only the results of the natural samples, since the comparison with the synthetic ones demonstrate the excellent quality of our natural magnetite.

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REFLECTIVITY MEASUREMENTS

We have performed optical reflectivity measurements of Fe_3O_4 as a function of the temperature (from 300 K down to 6 K), between 1 meV and 12 eV using four spectrometers. In the far-infrared region a Fourier spectrometer was employed using a He-cooled Ge bolometer as detector. All optical properties can be obtained through

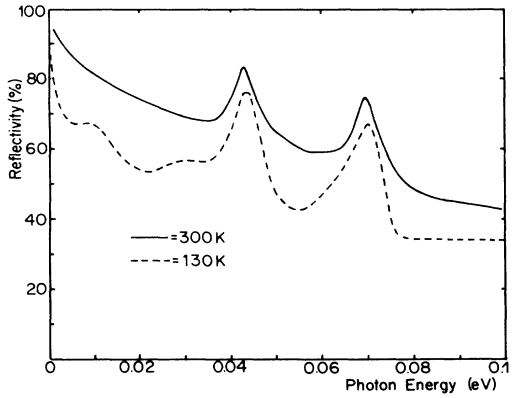

FIG. 1. Reflectivity spectrum of Fe_3O_4 at 300 K and at 130 K. (Hagen-Rubens extrapolation with dc conductivity of 24×10^{13} sec^{-1} and of 4×10^{13} sec^{-1}.)

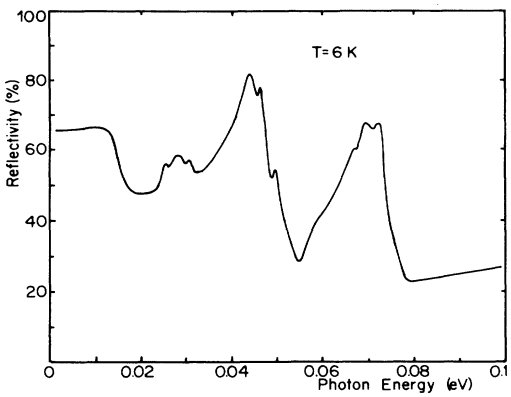

FIG. 2. Reflectivity spectrum of Fe_3O_4 at 6 K.

Kramers-Kronig transformations of the reflectivity data.[10]

We present the reflectivity measurements at room temperature (Fig. 1), as illustrated, and, for a more extensive discussion in relation to phonon modes, at 130 and 6 K (Figs. 1 and 2). Also, at 300 K (and also at 130 K) a Drude law is observed for the first time, confirming an early assumption of Schlegel *et al.*[3]

We have chosen the temperature of 130 K for two main reasons: first of all, at 130 K the sample has the lowest amount of free-charge carriers above the Verwey transition; we believe the free carriers to be the main cause of the "smearing" of the two low-energy phonons at room temperature (Fig. 1). Second, we are sufficiently above the Verwey temperature transition (120 K) to assume that the crystal structure of the sample has not changed, due to precursory effects of the phase transition.

The low temperature (6 K) measurement is performed with the aim to observe the effects of the crystallographic distortion of the Verwey transition on the phonon modes.

RAMAN MEASUREMENTS

We have also performed Raman scattering experiments on the same natural single crystal below and above the Verwey transition temperature. The sample was kept in a He cryostat in He atmosphere. The incident laser beam had a wavelength of 514 nm and 50 mW power.

The scattered light was analyzed by a double monochromator, the resolution of which was set to 8 cm^{-1}. Measurements were performed in a 180° backscattering geometry and the scattered light had a polarization which was 90° rotated relative to the incoming laser polarization.

DISCUSSION

The reflectivity spectrum at 130 K (Fig. 1) shows in the far-infrared energy range four main structures. The two peaks at high energy are identified with the phonon modes already known. There are now two quite broad and clearly resolved peaks at 0.012 and 0.032 eV, that we assert to be the last two phonon modes, as predicted by group theory for a structure with mainly cubic character.[5,6] In the past many investigations with infrared absorption spectroscopy, e.g.,[8,9] were carried out on the phonon modes; but the results concerning the phonons at low energies were unclear and contradictory. However, it must be noticed that our results agree very well with previous data reported in Ref. 9, even though we claim that the energy of the lowest mode is too high in Ref. 9.

The mode at 0.012 eV is, however, an average of several measurements. In fact at this energy we change in our measurements the detector: from 100 cm^{-1} down to 10 cm^{-1} we use a bolometer, that produces a non-negligible noise, and a small uncertainty in the absolute intensity.

At 130 K magnetite must still be considered as a conductor. This can be seen from the small plasma edge at very low energy. In order to extrapolate the reflectivity measurement towards 100% we have made use of the Hagen-Rubens law with a dc conductivity of 4×10^{13} sec^{-1}.[11]

Following Fig. 1, we note that the disappearing of the free-charge carriers as the temperature decreases makes the two low-energy-phonon modes sharper and sharper. At 130 K we have also performed a fit of the real part of the optical conductivity of the four phonon modes. The fits are based on the dispersion theory of Lorentz and consist of a sum of four Lorentzian curves and the Drude law for the free-charge carriers (plasma behavior) with a squared plasma frequency of 9×10^{-4} eV^2. The parameters of the fit are summarized in Table I. Figure 3 shows the final result, in fair agreement with the experimental data. At 6 K (Fig. 2) the four structures are more pronounced and clearly the low-energy behavior is a nonconducting one. For the three higher-energy phonon modes we detect a pronounced fine structure. In the lowest energy peak we cannot resolve the fine structure for the same reasons, as explained before for the spectrum at 130 K.

There is obviously a relation between these fine structures and the lattice distortion, due to the Verwey transition. Even though the problem of the crystal structure is far from the final goal, it is now clear that the Verwey transition cannot be explained only as a charge ordering in the *B* sites. Neutron and x-ray diffraction studies, e.g.,[12] disclosed that lattice distortions play an essential role. The aim of this paper is not to discuss in details the different models, explaining the Verwey transition, but to point out that these lattice distortions can be understood

TABLE I. Parameters for the four ir active phonon oscillators: ε is the energy, γ is the damping, and $4\pi Ne^2/\mu$ is the oscillator strength. The plasma frequency value is $\omega_p^2=9\times10^{-4}$ eV^2.

	Oscillator			
	I	II	III	IV
ε (eV)	0.012	0.032	0.0425	0.068
γ (eV)	0.0165	0.0130	0.0041	0.0079
$\frac{4\pi Ne^2}{\mu}$ (eV^2)	0.009 99	0.0079	0.0153	0.0194

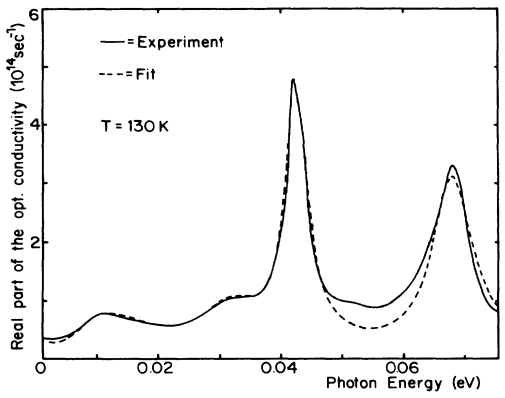

FIG. 3. Real part of the optical conductivity at 130 K (solid curve) with the theoretical fit, explained in the text (dashed curve).

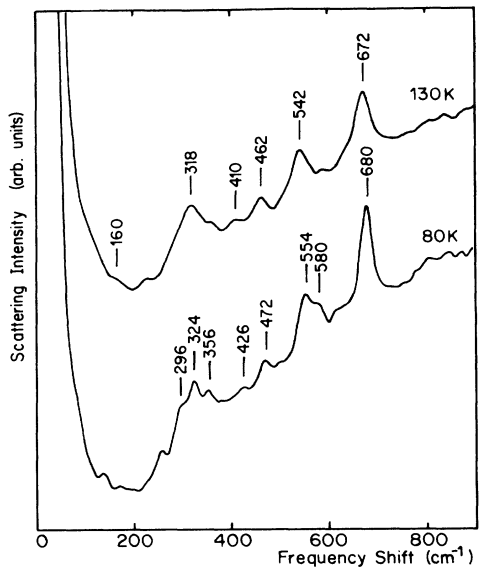

FIG. 4. Raman spectra at 130 and 80 K. The scattered light had a polarization which was 90° rotated relative to the incoming laser polarization.

as a small perturbation in the system. These perturbations of the mainly cubic structure, which nevertheless remains the most dominant lattice structure also below T_v, produce a splitting of the threefold-degenerate phonon modes (Fig. 2). Following these fine structures with decreasing temperature we note that they grow in intensity, and can be clearly distinguished from noise features. Finally, as support to our assertions, we remark that these fine structures of the phonon modes are typical and always present on all analyzed samples, natural and artificial ones.

Regarding now the Raman effect for temperatures above T_v five Raman active phonon modes are predicted. For temperatures $T > T_v$ (Fig. 4) only four of them are readily detectable, namely at 672, 542, 410, and 318 cm^{-1}. Neutron scattering experiments show the lowest lying Raman active mode to occur at 150 cm^{-1},[13] and indeed in some of our spectra we have found also a very weak excitation near 150 cm^{-1}. However, the band near 470 cm^{-1} has to be indexed as an optical magnon excitation which has been identified by Watanabe and Brockhouse[14] by means of neutron scattering experiments. Our experimental data are also quite well confirmed by the work of Hart *et al.*,[15] who identified the 470-cm^{-1} mode as due to magnon scattering. However, our measurements seem to confirm the neutron scattering results for the excitation near 150 cm^{-1}, in contrast to the 298-cm^{-1} peak of Hart *et al.*, which is absent in our spectrum. Polarization dependent measurements on an oriented, artificial single crystal revealed the peak at 672 cm^{-1} to be of A_{1g} symmetry. The mode at 318 cm^{-1} is a T_{2g} mode whereas the mode at 542 cm^{-1} might be of T_{2g} or E_g symmetry.

Cooling below T_v, it is shown in Fig. 4 that the 542-cm^{-1} excitation splits into at least two and the 318-cm^{-1} mode into three distinct peaks, while the phonon mode at 410 cm^{-1} shifts to higher energies but is much too weak to permit the observation of any splitting. Our symmetry assignment to the Raman active phonon modes, which show a splitting through the Verwey transition, is unambiguous, in contrast to earlier investigations,[15] where the symmetry assignment was a pure guess, since low-temperature measurements were missing.

It is thus the first time that changes in the phonon spectra below the Verwey transition temperature are observed by Raman scattering experiments, in contrast to early measurements by Verble.[16]

CONCLUSION

Because of our thorough investigation of the phonon modes of magnetite using a high-resolution spectrometer (FIR) and the Raman effect we are now able to bring more light into the effect of the Verwey transition on the phonon structure of magnetite, confirming also what, even up to now, was only a speculative prediction based on a group theoretical approach.

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