Optical Measurements on Magnetite

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The optical transmission of powdered single crystals of magnetite was measured in the spectral range from 200 to 4000 cm^{-1} at temperatures between 77 and 300 K. The measurements are compared with those on Ti-substituted magnetite. The spectrum of pure magnetite shows drastic changes at the Verwey transition. In the low-temperature phase, a small splitting up of the two high-temperature phonon bands is observed.

Most of the properties of magnetite show large variations at the so-called Verwey temperature ($T_V \approx 120$ K), which is caused by an electronic order-disorder transition on octahedral sites. Especially the electrical conduction behavior has been investigated extensively from an experimental, as well as from a theoretical, point of view. Several models have been proposed for the conduction mechanism above and below the transition. Cullen and Callen[1] introduced a Hamiltonian yielding overlapping bands above T_V which are separated below the transition temperature by an energy gap due to the intersite Coulomb repulsion of the electrons. Lorenz and Ihle[2] used the same Hamiltonian but started from localized carriers, and they were able to calculate the temperature dependence of the conductivity of magnetite. Also on the basis of this Hamiltonian an optical absorption peak of 0.11 eV was predicted; passing through the Verwey transition, the intensity of this peak should change. They claimed that this peak had been observed by Balberg and Pankove[3] at 0.16 eV. However, these authors themselves attribute this absorption to the impurities of the natural crystals which were used. Recently, the present authors[4,5] reported the thermoelectric properties of very pure and Ti-doped synthetic magnetite single crystals and explained the behavior of the Seebeck coefficient below T_V on the basis of a simple model of thermally activated conduction over two energy levels separated by a gap of about 0.12 eV, which is created at the transition. Within this model one would expect an absorption peak below T_V near 0.12 eV which would disappear above the transition.

However, up till now no clear evidence of such drastic changes predicted on the basis of various models have been observed in the published optical spectra. Unfortunately, a number of reported spectra concern only the spectral range above 0.15 eV[3,6] and others concern the lattice vibrations well below 0.10 eV.[7,8] The absorption spectrum in the appropriate range reported by Waldron[9] showed at room temperature stronger absorption than at 80 K, but no evidence of a sudden change at T_V was reported. Similar features were observed in the reflection spectra by Buchenau and Müller[10] and Samokhvalov, Tutikov, and Skornyakov[11]; only small changes in the spectra occurred at the Verwey transition, larger changes took place at temperatures well above T_V and at energies significantly larger than 0.1 eV. In our opinion the absence of substantial changes at T_V around the photon energy 0.1 eV could be due to the impurity and nonstoichiometry of the specimens which were used for the measurements (e.g., natural single crystals). In view of this, the optical absorption of very pure and Ti-substituted magnetite was investigated in the spectral range from 0.5 to 0.025 eV.

For the present study we have used synthetic magnetite crystals, which were grown from presintered bars of spectroscopically pure $Fe_2O_2(6N)$ by means of a floating-zone technique in an optical furnace. After preparation the crystals were annealed for 70 h at 1130°C in a CO_2-H_2 mixture with an oxygen partial pressure of $\log_{10}P_{O_2} = -10.2$. During cooling to room temperature the CO_2-H_2 ratio was changed in such a way that stoichiometric magnetite crystals were obtained.[12] According to the thermoelectric power measurements,[4] the deviations from stoichiometry of these crystals are within 100 ppm. In a similar way, single crystals of highly pure $Fe_{3-x}Ti_xO_4$ with $x = 10^{-3}$, 0.1, and 0.2 were prepared.[13] Transmission measurements were performed on powdered single crystals by means of the KBr-pellet technique. A double-beam infrared spectrofotometer was used. The measurements were carried out between liquid-nitrogen and room temperatures. The concentration of absorbing material in the pellets was about 0.8 mg/cm².

In Figs. 1(a) and 1(b) the transmission of KBr pellets with Fe_3O_4 and $Fe_{2.8}Ti_{0.2}O_4$ is plotted in

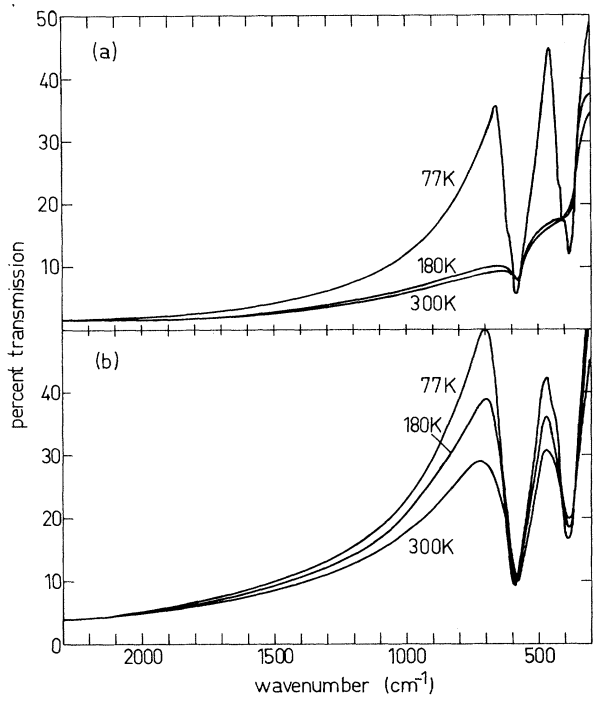

FIG. 1. The relative transmission vs wave number at three temperatures. (a) Fe_3O_4; (b) $Fe_{2.8}Ti_{0.2}O_4$.

the range from 2300 to 300 cm^{-1} with the temperature as parameter. The spectra of Ti-doped magnetite with $x = 10^{-3}$ were nearly identical with those of pure magnetite, while the specimen with $x = 0.1$ showed roughly the same behavior as that with $x = 0.2$. A kind of absorption edge near 1000 cm^{-1} is observed in the low-temperature phase of magnetite, as well as in Ti-substituted magnetite with $x = 0.1$ and $x = 0.2$, in the whole temperature range.

In order to show more clearly that in magnetite the change in the spectrum is really induced by the Verwey transition, we recorded the transmission at 675 cm^{-1} as a function of temperature. During this measurement a 10-μm filter was used to prevent heating of the sample. The results are plotted in Fig. 2 from which it can be seen that the absorption shows an abrupt change near T_V. In the case of Ti-substituted magnetite with $x = 0.1$ and $x = 0.2$, a gradually increasing absorption with temperature was found; in these compounds, the jump in the electrical conductivity was absent.

The high absorption observed above 1000 cm^{-1} (0.12 eV) in magnetite is qualitatively in accordance with previous measurements.[3,6,10] Actually, zero optical conductivity at 0.11 eV was predicted

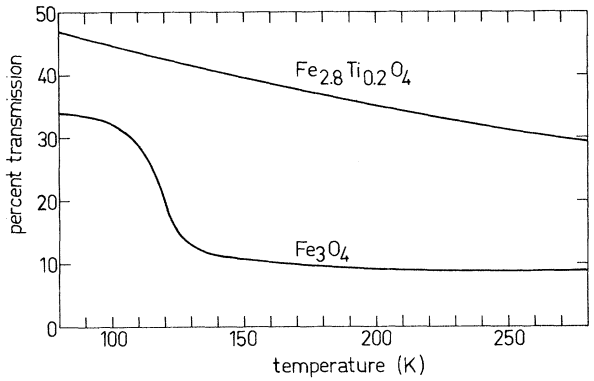

FIG. 2. The relative transmission vs temperature at 675 cm^{-1} of Fe_3O_4 and $Fe_{2.8}Ti_{0.2}O_4$.

by Buchenau and Müller[10] by means of extrapolation of measurements at higher energies, but they did not establish the sudden disappearence of this zero conductivity at T_V.

It is noticed that a high degree of similarity exists between the low-temperature spectra of pure and Ti-substituted magnetite (Fig. 1). In view of this we came to two possible explanations for the absorption edge. Firstly, it can be argued that also in the compounds with $x = 0.1$ and $x = 0.2$, where disorder occurs due to the presence of Ti^{4+} ions, a gap is formed at the Fermi level because of the Coulomb repulsion of the electrons.[14] The formation of such a gap in disordered systems is not accompanied with a first-order phase transition as in pure magnetite. A second possibility is that this vanishing absorption at low frequencies is a result of localization of the charge carriers.[15] In magnetite this localization would be due to correlation only, while in Ti-substituted magnetite it would be caused by both correlation and disorder.

In addition to the above-mentioned substantial changes in the spectrum of magnetite at the Verwey transition, we found a small splitting up of the two high-temperature absorption bands (570 and about 380 cm^{-1}) into five absorptions below T_V at 615 and 585, and at 420, 405, and 375 cm^{-1}, respectively. This effect was absent in Ti-substituted magnetite with $x = 0.1$ and $x = 0.2$ in which the Verwey transition also does not occur. In Fig. 3 details of the infrared spectra at liquid-nitrogen temperature are given. An excessive splitting is not observed, which is conceivable regarding the small lattice distortions at the transitions.[16] Nevertheless, the symmetry of the crystal is lowered which gives rise to breaking of the selection rules and, consequently, to an

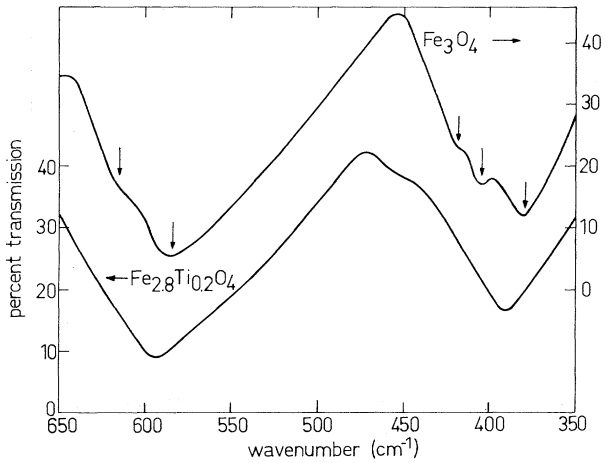

FIG. 3. Details of the spectrum of Fe_3O_4 and $Fe_{2.8}Ti_{0.2}O_4$ at 77 K. The splitting of the bands is indicated by the arrows.

increasing number of infrared- and Raman-active modes.

These results are in contradiction to the light-scattering experiments by Verble[17] by means of Raman spectroscopy. Passing through the Verwey transition he observed no dramatic changes in the Raman spectra and found only line broadening. The absence of the phonon-band splitting and drastic changes at T_V in the data of Verble may be explained by the experimental conditions. Our infrared spectra were recorded on powdered single crystals, i.e., on cleaved surfaces. Moreover, the purity and stoichiometry of these crystals is assumed to be very good.[4,5] Verble's data were obtained on mechanically polished, single-crystal surfaces. The distorted surface layer may be in the order of the skin effect of the radiation used. Apart from this, no differences were observed by Verble between natural and synthetic single crystals. Usually, natural single crystals contain impurities up to 1% and sometimes even more; synthetic single crystals may be highly nonstoichiometric. Both effects will have a large influence upon the low-temperature phase of magnetite[4,5] even at concentrations well below 1%. For this reason the infrared spectrum of Ti-doped magnetite with $x = 10^{-3}$ was measured and, even at this small concentration, the fine structure was found to be less pronounced than in the case of the pure material.

In conclusion we may say that the reported optical measurements do show drastic changes at T_V as is expected from several models.[1,2,4] The reason that, until now, rather poor evidence of such changes in the optical spectrum was found is, in our opinion, due to the use of nonstoichiometric and impure samples and to searching in the wrong spectral range. The origin of the absorption edge is not yet completely understood, considering the close similarity of the magnetite spectrum with that of Ti-substituted magnetite. The fine structure below T_V in the phonon spectrum is, to our knowledge, reported for the first time and is largely in accordance with what would be expected from the structural distortion.

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