Optical Measurements on Magnetite Single Crystals*

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Optical transmission and reflectance were measured on natural magnetite single crystals in the spectral range $0.15 \lesssim h\nu \lesssim 0.75$ eV. These measurements below and above the semiconductor-to-metal transition temperature T_V have shown that, unlike for the vanadium oxides, there is no collapse of the optical gap at the transition. The present results and the existing data on the transport properties of magnetite indicate that different bands contribute to the electric conduction above and below T_V.

Magnetite, Fe_3O_4, is one of the early materials for which it was realized that the Wilson band theory does not apply,[1] and it is the first material in which a semiconductor-to-metal phase transition was found.[2] This transition takes place at the so-called Verwey temperature, $T_V = 119°K$. While many studies on the electrical and magnetic properties of this material have been made,[3,4] very few and limited optical data are available for this material.[5-7] Only room-temperature reflectivity has been studied so far on single crystals,[5] while optical absorption studies were carried out only on films[6] (for photon energies $h\nu > 1.5$ eV) and powders[7] (for $h\nu \lesssim 0.2$ eV). Furthermore, no optical constants were determined.

In magnetite the spin-down d bands can be regarded as fully occupied and well separated from spin-up d bands. These spin-up bands are split by the crystal field into two doublets and one low-lying singlet band. This singlet band should be half filled and thus yield metallic behavior.[8] However, for $T < T_V$ magnetite exhibits a semiconducting behavior, and an energy gap due to interatomic correlation energy[3,10] is expected[10,14] to split up this singlet band. We shall call this energy gap, E_{MW}, the Mott-Wigner (MW) energy gap, and the corresponding bands that emerge, the MW valence band and the MW conduction band. As the energy E_{MW} is expected[12,14] to be within the previously unexplored optical range and as the largest measured[3,12,14] conductivity-activation energy in the purest magnetite crystals just below T_V is 0.15 eV, it appears that the spectral range $1.5 \gtrsim h\nu \gtrsim 0.15$ eV should be studied. Furthermore, to understand the nature of the transition it is extremely important to study the optical properties in this spectral range above and below the transition temperature. There is no earlier determination whether an optical energy gap is or is not produced when the material is cooled below the transition tempera-

ture, while theoretical models for this material are strongly dependent on the formation of an energy gap.[4,8,12] In V_2O_3 and VO_2, investigations below and above the transition temperature have shown that at the transition, the optical band gap had collapsed.[15-18] As we shall see below, the case of Fe_3O_4 is different and therefore appears to be the first transition-metal oxide that exhibits the semiconductor-to-metal transition while the optical measurements do not indicate any band overlap.

For the present study, we have used natural magnetite single crystals. The lattice constant of the crystals is 8.396 ± 0.001 Å, and their main impurities are Ti (≈ 1.0 wt%) and Zn (0.15 wt%) while the total content of the other metallic impurities was about 0.1%. The crystals were cut into slices, the planes of which were perpendicular to the crystallographic [111] direction. These slices were polished down to 50 or 25 μm and cemented to a CaF_2 wafer.

In Fig. 1 we show the typical temperature dependence of the conductivity of the actual samples used for the optical measurements. This dependence is similar to that observed in the many earlier studies.[3,4,19] The activation energy increases from 0.05 eV at very low temperature to about 0.1 eV just below the transition and is 0.04 eV just above the transition. This 0.04-eV value seems to be independent of sample purity.[6,14,20]

For the optical measurements, the sample was placed on an apperture. Transmission measurements were made by the sample-in, sample-out technique in which the sample-out condition consisted of replacing the mounted specimen by an identical CaF_2 wafer without magnetite.[14]

The optical relative transmission I/I_0, the reflectance R, and the absorption constant α are related by

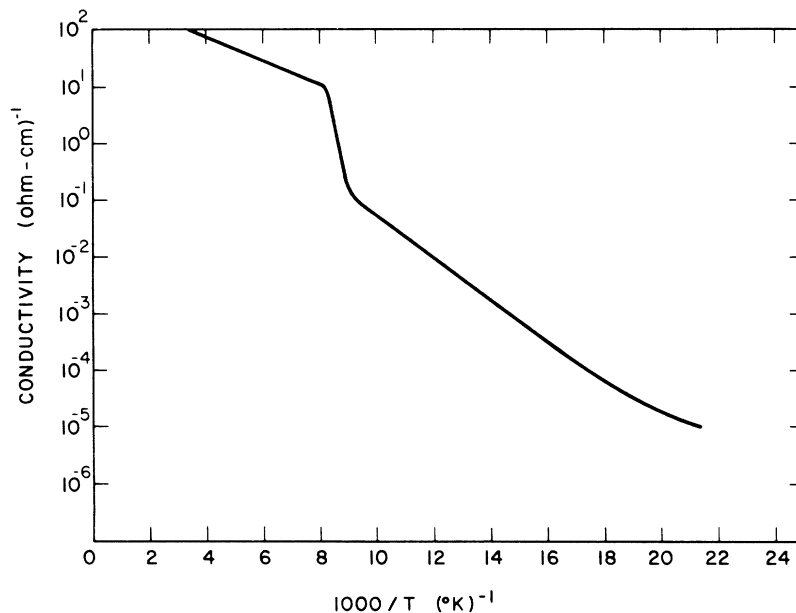$$I/I_0 = (1 - S)(1 - R)^2 \exp(-\alpha d), \qquad (1)$$

FIG. 1. The conductivity dependence on temperature of crystals used for the optical measurements.

where S is the fraction of light scattered and d is the thickness of the sample. In Fig. 2 we show the results of the measurements of I_0/I and R as functions of the incident photon energy for a 25-μm-thick sample and the α deduced from these results using Eq. (1). The results shown in Fig. 2(a) indicate that the absorption edge starts at about 0.3 eV and rises slowly to higher energies. The actual absorption edge is expected to rise faster than shown in Fig. 2(a) as can be seen if one subtracts the contribution of those absorption processes which cause the absorption to increase with decreasing photon energy and which are dominant below 0.3 eV. As for V_2O_3,[15,16] the broad absorption edge is probably due to band tails that are expected to be formed by imperfections and strong correlation effects.[21] Two sharp absorption peaks are observed at 0.16 and 0.21 eV; their origin is not understood, but it is conceivable that these peaks may be associated with the Ti and Zn impurities. The most striking and important result is the fact that only very *minor* changes in the absorption spectrum are observed while passing through the transition temperature, in significant contrast to the behavior of the vanadium oxides. This fact will be discussed below. No significant difference was observed between different samples.

Because of the strong absorption above $h\nu = 0.75$ eV, we were unable to measure the transmission above this energy in single-crystal samples. Using an Fe_3O_4 film we have extended the transmis-
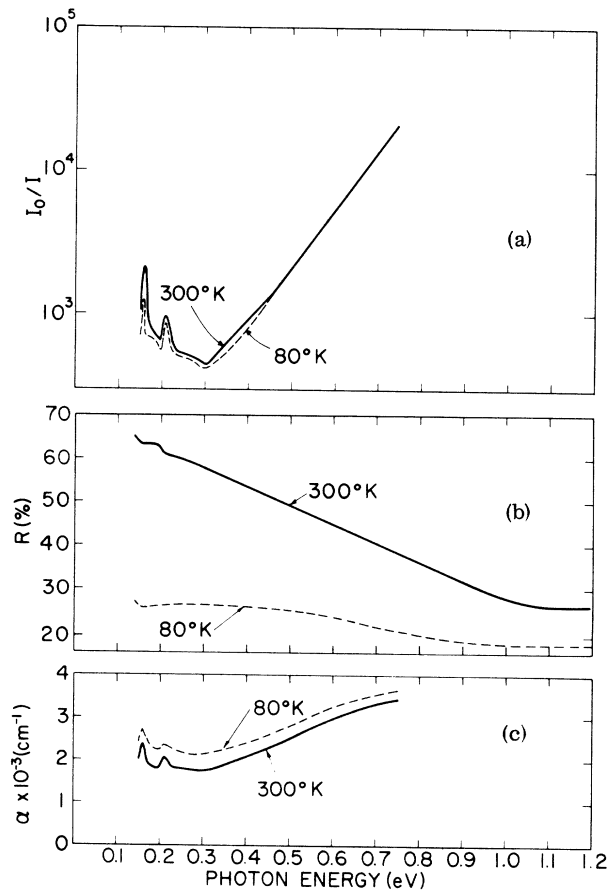

FIG. 2. (a) The reciprocal of the measured relative transmission and (b) the reflectivity of a 25-μm-thick, natural magnetite crystal. (c) The absolute absorption coefficient, obtained from (a) and (b).

sion measurements to the $0.5 \leq h\nu \leq 4$ eV range.[14] Again no significant change was found by cooling the sample from 300 to 80°K. The film absorption was similar[14] to that reported by Miles, Westphal, and von Hippel.[6]

In Fig. 2(b) we show the magnetite reflectance versus incident photon energy, as compared with that of evaporated Al, for 300 and 80°K. Our results are in good agreement with the earlier measurements of the reflectance spectra of ferrites at room temperature[5] and with the dependence of the reflectance in these materials on their conductivity. The reflectance dependence on the wavelength, and the agreement with the results obtained with ferrites, indicate that the main contribution to the 300°K reflectance is due to "free" carrier absorption while at 80°K the main contribution is due to interband transition. We put the word free in quotes because one may interpret[5,22,23] the 300°K reflectance[5] of magnetite and its transport properties[22,23] as indicating that above T_V small polarons are formed.[12]

As S was determined to be less than 10% and as the results are in good agreement with previous reflectance measurements, we did not make a correction for S when using Eq. (1) to calculate α from the results shown in Figs. 2(a) and 2(b). These values of α are shown in Fig. 2(c). They are in the range that one would expect[9] for d-band to d-band transitions and are very close to the results[15] obtained with semiconducting V_2O_3.

In view of the many absorption processes that can take place in the spectral range under study,[9] the relatively weak absorption due to the d-band to d-band transitions, and the lack of published data for optical and transport properties we can only analyze the gross features of the data obtained. It is well established from the many conductivity measurements that the conductivity activation *gap* drops from 0.3 to 0.08 eV at T_V. From the present results we know that the optical gap does not change through the transition and thus we conclude that the optical gap is not the conductivity gap above the transition temperature. From the following discussion it appears that there are good reasons to believe that the activation energy just below T_V corresponds to the observed optical gap while the activation energy just above T_V corresponds to the value of E_{MW} just above T_V. This in turn sheds light on the thermoelectric-power and the Hall-effect data as will be discussed below.

We propose that 0.3 eV correspond to transitions between the MW valence band and a "broad-

er" band. In view of the α values obtained, the "broader" band is likely to be the lowest-lying spin-up d-doublet band.[8] The conductivity in this band is more bandlike (and thus we may call it "broader") in contrast to that of the MW bands, and thus this "broader" band contributes most to the conduction for $T < T_V$. That the d-doublet band has a bandlike conduction is not unexpected in view of the effect of degeneracy on conduction in narrow bands.[24] At the transition, E_{MW} collapses from its unknown value below T_V to about 0.08 eV and the main contribution to the conduction is due to the rather narrow MW conduction band. If polarons are formed,[12,22] E_{MW} is smaller than this value. Above T_V, the gap E_{MW} continuously decreases with increasing temperature.

There are four pieces of evidence that support the above interpretation: (1) Lavine[20] found that the thermoelectric power above the transition increases with temperature and this was interpreted[22,23] as due to conduction in a narrow band. This and the fact that Siemons[25] found the same value of thermoelectric power for 77 and 300°K indicate that this power decreases with temperature for $T < T_V$ and bandlike conduction is dominant in this temperature regime. (2) Siemons found that for $T < T_V$ the Hall mobility decreases with temperature, it drops through the transition, and then for $T > T_V$ it increases with temperature in agreement with (1) and with our suggestion. (The low Hall mobility for $T < T_V$ is due to carrier scattering due to optical phonons that might make the measured Hall mobility much smaller than the drift mobility.[9]) (3) In contrast to V_2O_3 and VO_2,[4] the conductivity of Fe_3O_4 increases with increasing temperature above T_V and the sharp collapse of the activation energy at T_V is followed by a continuous shrinkage of this energy as the temperature increases. (4) Our proposed interpretation is very much in accord with the band model of Cullen and Callen[8] and the experimental evidence on which it is based. According to their model, the correlation gap should be *indirect* and since the absorption due to other processes has an α of the order of 10^3 cm^{-1} it should not be seen by the present optical measurements. The possible physical reasons for the collapse of the activation gap and their connection to the Cullen and Callen[8] model will be discussed elsewhere.[14]

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Precise Proton-Polarization Standards Determined with a Lamb-Shift Ion Source Incorporating a Nuclear Spin Filter*

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The polarization of an 8–12-MeV proton beam produced by a Lamb-shift ion source has been determined with 0.4% absolute accuracy by an atomic-beam technique. The procedure, which involves selection of a single hyperfine state of fast H(2s) atoms, is ideally suited to routine monitoring of beam polarization. Absolute p-^{4}He elastic-scattering analyzing powers measured with the calibrated beam are reported, and existing double-scattering data are compared with these results.

The purpose of this Letter is twofold. First, we describe an atomic-beam method for accurately determining the polarization of protons produced by a Lamb-shift polarized-ion source incorporating a nuclear spin filter.[1] Second, we present absolute analyzing powers for p-^{4}He elastic scattering which were obtained with the calibrated proton beam, at several energies and angles coinciding with the most precise existing double-scattering data.[2,3]

In a Lamb-shift polarized-ion source, H(2s) atoms are produced by charge transfer of 500-eV protons in cesium vapor; these are subsequently converted to H$^-$ ions by charge transfer in argon gas. In the Los Alamos apparatus,[4] a nuclear spin filter is located between the cesium and argon cells. This is a resonant interference

device which can be tuned (by adjusting its axial field B) to pass only H(2s) atoms with nuclear magnetic quantum number $m_I = +\frac{1}{2}$. These atoms produce a H$^-$ beam which has 100% nuclear polarization, independent of the magnetic field strength in the ionization region. The formation of H(1s) atoms, a small fraction of which convert to H$^-$ ions, contributes a (nominally) unpolarized background beam whose magnitude is about 10% of the total output current.

The procedure for determining the beam polarization (called the "quenching-ratio method") consists simply of measuring the normal output current i and the background current i_B which remains when all H(2s) atoms are quenched to the ground state.[5] The beam polarization is then expected to be $p_Q \equiv (i - i_B)/i$ since the component