

## Electrical and Optical Properties of FeO\*

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Single crystals of  $\text{Fe}_{1-x}\text{O}$ , where  $0.05 < x < 0.15$ , have been grown by chemical vapor deposition. Optical absorption measurements indicate two Jahn-Teller-split  $\text{Fe}^{2+}$  crystalline-field peaks and an absorption edge near 2.4 eV, independent of stoichiometry. The latter is interpreted as due to a transition from a localized  $3d$  electron to the  $4s$  band. Infrared reflectivity measurements are also reported. Electrical conductivity of  $\text{Fe}_{0.91}\text{O}$  was measured from 20 to 300 K. The activation energy above 120 K was 0.07 eV. In the region from 100 to 120 K, the activation energy increased to 0.14 eV, strongly indicating both band-like conduction and partial compensation. From 20 to 100 K, the logarithm of the conductivity is proportional to  $T^{-1/4}$ , behavior indicative of the predominance of phonon-assisted tunneling of trapped holes in the vicinity of the Fermi energy. The data are consistent with band-like conduction in the oxygen  $2p$  band in parallel with small-polaron hopping in the  $\text{Fe}^{2+} 3d^6$  band.

### I. Introduction

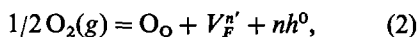
The electronic structure of transition-metal oxides has been a matter of great interest for many years (1-3), but few firm conclusions have been reached. It is fairly clear that the sequence of materials MnO, FeO, CoO, and NiO are all Mott insulators, but FeO has not been investigated as thoroughly as the others in this interesting group. A major reason for this is the fact that the stoichiometric composition does not appear within the homogeneity range, which extends from  $\text{Fe}_{0.95}\text{O}$  to  $\text{Fe}_{0.85}\text{O}$ . In addition, the material is unstable below 840 K, phase separating into  $\alpha\text{-Fe}$  and  $\text{Fe}_3\text{O}_4$ . Nevertheless, several electrical studies have been reported (4-8), and the high-temperature conduction properties have been determined. In particular, the variation of electrical conductivity with temperature and oxygen partial pressure,

$$\sigma \propto P_{\text{O}_2}^{1/n} \exp(-E_a/RT - \bar{H}_{\text{O}_2}/nRT), \quad (1)$$

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has been studied to determine the nature of point defects and the conduction mechanism. A series of studies by Wagner and his students (6-8) have shown conclusively that, at high temperatures, the source of free holes is the ionization of iron vacancies,



and that  $1/n \rightarrow 1/6$  at high temperatures and small values of nonstoichiometry. The activation energy for conduction varies from 0.18 eV at  $\text{Fe}_{0.95}\text{O}$  to 0.05 eV at  $\text{Fe}_{0.85}\text{O}$  (8). The large defect concentrations are known to result in defect clustering or agglomeration, necessitating a more complex expression than Eq. (2).

The thermodynamics of the system has also been comprehensively studied and recently reviewed (9). The partial molar heat of solution of a molecule of oxygen into  $\text{Fe}_{1-x}\text{O}$  is  $\bar{H}_{\text{O}_2} = 2.65$  eV.

Many questions remain to be answered about transport in  $\text{Fe}_{1-x}\text{O}$ . It is not yet known whether the predominant conduction mechanism is via the hopping of small polarons

or the band-like motion of large polarons. The temperature dependence of the mobility has not been determined, and it is not known if the conducting holes move predominantly in the cation  $3d$  band or the anion  $2p$  band. In addition little has been reported about the optical properties.

## II. Experimental Methods

Single crystals of wustite were prepared at  $750^\circ\text{C}$  by closed-tube chemical vapor deposition onto MgO substrates (10). Optical-absorption measurements (Cary (14)) were made on very thin as-grown samples ( $<10\ \mu\text{m}$ ). The composition (O/Fe) was established by postgrowth anneals in  $\text{CO}_2/\text{CO}$  gas mixtures. Electrical conductivity and ir reflectivity (Beckman IR-12) measurements were made on thicker specimens ( $>100\ \mu\text{m}$ ) which had been removed from the substrates. Platinum wire contacts were fixed onto the conductivity samples at  $800^\circ\text{C}$  (in  $\text{CO}_2/\text{CO}$  atmosphere) in order to obtain ohmic contacts. Since thin specimens were used, the van der Pauw sample configuration was used to measure conductivity and Hall mobility. Two different external circuits were used on two different samples to check the reproducibility as the resistivity increased at low temperatures. The shape of the curves were identical. The sample composition was checked by X-ray measurements. No  $\text{Fe}_3\text{O}_4$  could be detected from Debye-Scherrer measurement on quenched wustite samples. Transmission electron microscopy also revealed no second phase although satellite reflections corresponding to the ordering of defects were observed in electron-diffraction patterns, in agreement with previous results (11).

## III. Optical Properties

The ir reflectivity curve for  $\text{Fe}_{0.93}\text{O}$  is shown in Fig. 1. The main Reststrahl peak is near  $410\ \text{cm}^{-1}$ , with a side band appearing at about  $570\ \text{cm}^{-1}$ . The main peak decreases in wave number as the nonstoichiometry is increased, shifting to approximately  $380\ \text{cm}^{-1}$  for  $\text{Fe}_{0.91}\text{O}$ . The peaks are much broader than in more stoichiometric transition-metal

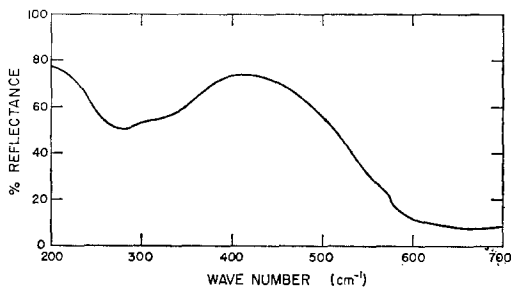


FIG. 1. Reflectance as a function of photon wave number for a single crystal of  $\text{Fe}_{0.93}\text{O}$ .

oxides, as would be expected from the large amount of disorder in  $\text{Fe}_{1-x}\text{O}$ .

The optical absorption from 0.7 eV to 2.8 eV is shown in Fig. 2. Broad crystalline-field absorption occurs between 1.0 and 1.5 eV, with two distinct peaks near 1.1 and 1.4 eV evident in the more nonstoichiometric samples. Resolution was not improved at 77 K. As the excess-oxygen concentration increases, absorption increases and the 1.1 eV peak is accentuated. The absorption coefficient,  $\alpha \approx (1/d)\ln(I_0/I)$ , is of the order of  $10^4\ \text{cm}^{-1}$  for the maximum crystalline-field absorption. Two crystalline-field peaks associated with  $\text{Fe}^{2+}$  have previously been observed in the (Fe, Mn)O system (12) as well as in the  $\text{Fe} \cdot (6\text{H}_2\text{O})^{2+}$  complex (13), and were attributed to a dynamical Jahn-Teller splitting.

All samples exhibited a fundamental absorption edge near 2.4 eV. This value is considerably below the edges previously reported in MnO, CoO, and NiO, all of which are in the 3–5 eV range. We feel that this is a real effect rather than a consequence of the large degree of disorder in  $\text{Fe}_{1-x}\text{O}$ . Experimentally, the edge is quite sharp, particularly in the more stoichiometric samples, and it does not shift with composition. In NiO, the fundamental edge has been attributed to a transition from an electron in a  $3d^8$  configuration to the cation  $4s$  band (14), although others (15, 16) suggest it is a  $2p \rightarrow 3d$  transition. If the former process were responsible for the edge in  $\text{Fe}_{1-x}\text{O}$ , it would correspond to the free-ion reaction,  $3d^6 \rightarrow 3d^5 4s$ . Since  $3d^5$  is a half-filled shell configuration, this process requires less energy than the analogous processes in MnO, CoO, or NiO;

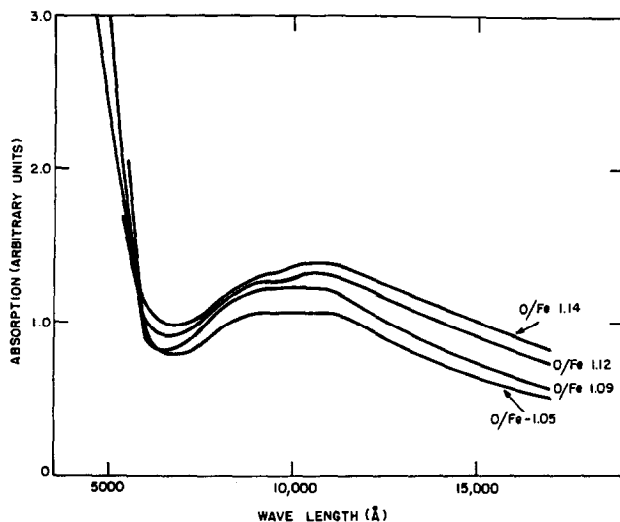


FIG. 2. Logarithm of the absorption constant as a function of photon wavelength for several samples of  $\text{Fe}_{1-x}\text{O}$  of different stoichiometries.

in particular, only 3.8 eV is necessary for the minimum-energy transition in FeO, as compared to 6.7 eV in NiO. It is thus not surprising that the edge is significantly lower in FeO than in NiO. The remarkable fact that the observed absorption edge is approximately 60% of the minimum free-ion  $3d^n \rightarrow 3d^{n-1} 4s$  energy in all four materials is strong evidence that it represents a  $3d \rightarrow 4s$  transition in each case.

#### IV. Electrical Conductivity

Figure 3 shows the observed electrical conductivity in  $\text{Fe}_{0.91}\text{O}$ , and compares it to earlier work of Tannhauser (4) on FeO and  $\text{Fe}_3\text{O}_4$ . The previous data indicate that some precipitation of  $\text{Fe}_3\text{O}_4$  may have occurred in the polycrystalline wustite, since the rapid increase of conductivity near 125 K is suggestive of the semiconductor-metal transition in the latter material. The single crystals studied here should be less likely to undergo phase separation, and in fact showed no signs of this in electron-diffraction experiments. The present measurements extrapolate precisely to the high-temperature results of Hillegas (8), having both the same activation energy (0.07 eV) and preexponential factor ( $\sim 300 \Omega^{-1} \text{cm}^{-1}$ ). Below 120 K, the activation

energy doubles, to 0.14 eV, and below 100 K, no true activation energy can be defined. As shown in Fig. 4, the logarithm of the conductivity from 20 to 100 K is proportional to  $T^{-1/4}$  rather than  $T^{-1}$ . This behavior was first predicted by Mott (17) for the phonon-

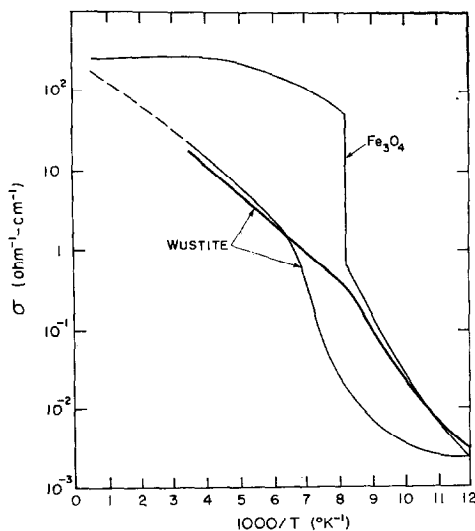


FIG. 3. Electrical conductivity as a function of reciprocal temperature for a single crystal of  $\text{Fe}_{0.91}\text{O}$ . The data of Tannhauser (4) for both FeO and  $\text{Fe}_3\text{O}_4$  are shown for comparison. — Tannhauser; — present work.

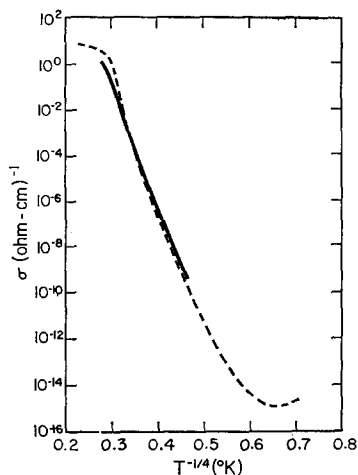


FIG. 4. Electrical conductivity plotted as a function of the inverse fourth root of temperature for a single crystal of  $\text{Fe}_{0.91}\text{O}$  (— wustite). The data of Drabble et al. (19) on  $\text{Fe}_3\text{O}_4$  are shown for comparison. (---).

assisted tunneling of carriers near the Fermi energy of a disordered system at sufficiently low temperatures. No Hall voltage could be detected at either 77 or 300 K.

The electrical conductivity behavior is quite similar to that observed in Li-doped NiO (14). It can be concluded that  $\text{Fe}_{0.91}\text{O}$  is a partially compensated semiconductor where the compensating defects are either oxygen vacancies formed during growth or trivalent impurities such as  $\text{Cr}^{3+}$  or  $\text{Al}^{3+}$  present on cation sites. At low temperatures, the Fermi level then lies in the narrow acceptor band, and the activation energy for free-hole conduction is just the difference between the acceptor energy and the top of the valence band. Above the temperature at which the free-hole concentration equals the density of compensating donors, the Fermi level moves down to a point approximately halfway between the acceptor band and the top of the valence band, and the activation energy thus halves. At still higher energies, intrinsic conduction should eventually predominate, but such a region has never been observed in FeO. (As further evidence that transport is extrinsic in the 120–1000 K range, we note that the preexponential factor in the conductivity is only  $300 \Omega^{-1} \text{cm}^{-1}$ , significantly lower than

would be expected for intrinsic conduction).

Below 100 K, a parallel conduction mechanism predominates. The  $T^{-1/4}$  behavior indicates that it represents variable-range hopping of a localized hole near the Fermi energy. Although such behavior can result from other mechanisms (18), variable-range hopping is completely plausible in  $\text{Fe}_{0.91}\text{O}$  at low temperatures. The system is highly disordered, having 9% cation vacancies and thus 18%  $\text{Fe}^{3+}$  sites. The compensation present requires the Fermi energy to lie in the acceptor band below 120 K. Furthermore, the data of Drabble et al. (19) on  $\text{Fe}_3\text{O}_4$  shown in Fig. 4, although quite similar in magnitude to the results on  $\text{Fe}_{0.91}\text{O}$ , clearly do not follow a  $T^{-1/4}$  law over any significant range; on the other hand, the  $\text{Fe}_{0.91}\text{O}$  data are linear over a range of a factor of  $10^7$  in conductivity.

Insufficient information is available to decide with certainty whether the free-hole conduction is primarily in the anion  $2p$  band, as has been suggested in the case for Li-doped NiO (14), or in the cation  $3d^6$  band. However, with 9% cation vacancies present, it is virtually certain that complete paths through the crystal exist in which each cation is nearest neighbor to a vacancy site. Thus, free-hole conduction in the  $3d^6$  band should either proceed without activation or with only the small-polaron hopping energy, depending on the spatial extent of  $3d^6$  polarons. The fact that ordinary band-like conduction in a partially compensated material appears to be the simplest explanation of the data is then strong indication that the free holes move in the oxygen  $2p$  band.

## V. Conclusions

The electronic structure of FeO appears to be very similar to that of NiO. The optical absorption is dominated by a relatively sharp edge at 2.4 eV and a broad, Jahn-Teller-split crystalline-field peak near 1.3 eV. The edge appears to result from excitation of a localized  $3d$  electron into the  $4s$  band. Electrical conductivity at low temperatures is primarily variable-range, phonon-assisted hopping near the Fermi energy. Above 100 K, free-hole conduction predominates. The material is

partially compensated by a small concentration of donors. There is evidence that the free holes move in the oxygen  $2p$  band.

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