Pressure dependence of the Verwey transition in magnetite: An infrared spectroscopic point of view

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I. INTRODUCTION

Numerous experimental studies have been carried out on the natural mineral magnetite (Fe₃O₄) to understand its puzzling electronic and magnetic properties. It is the oldest known magnetic material and the prototype material for the Verwey transition, which leads to charge ordering.¹ Fe₃O₄ has an inverse cubic spinel structure at ambient conditions and is in a mixed-valence state described as [Fe³⁺]₆[Fe²⁺]₂[Fe³⁺]₁₈O₄, where A and B denote the tetrahedral and octahedral sites, respectively, in the spinel structure AB₂O₄, with space group Fd3m.² At ambient conditions, magnetite can be classified as a bad metal due to the presence of a small Drude contribution.³–⁵ With decreasing temperature, magnetite undergoes a metal-to-insulator transition at the so-called Verwey transition temperature Tᵥ ≈ 120 K, concurrent with a lowering of the crystal structure symmetry from cubic to monoclinic.⁶–⁹ Various experimental investigations led to contradictory scenarios for the rearrangement of charges on the Fe sites and the resulting charge ordering below Tᵥ.¹⁰–¹⁵ In contrast, consistent results have been obtained by various groups regarding the changes in the optical properties when cooling below Tᵥ: According to infrared reflectivity measurements as a function of temperature, a clear opening of a charge gap (≈0.14 eV) and the appearance of numerous infrared modes due to the crystal symmetry lowering were observed.

Besides the charge ordering pattern below Tᵥ, a matter of controversy is furthermore the behavior of Tᵥ as a function of pressure. Resistivity measurements¹⁶,¹⁷ showed a sharp drop of Tᵥ at the critical pressure Pᵥ ≈ 7–8 GPa to zero and a metallization above Pᵥ. This finding was confirmed later on by ac magnetic susceptibility together with resistivity measurements.¹⁸ In Ref. 18, furthermore the existence of a quantum critical point in the pressure-temperature phase diagram of magnetite was claimed.¹⁸ In contradiction to these results, several groups found a linear decrease of Tᵥ with increasing pressure based on resistivity measurements, with a linear pressure coefficient of either −2.8 K/GPa¹⁹–²¹ or −5 K/GPa.²²,²³ A recent Raman study confirmed the linear decrease of Tᵥ with −5 K/GPa.²⁴ The absence or presence of a quantum critical point could be related to the level of hydrostaticity in the pressure cell, which may vary for the different types of experiments. Also, the measurement technique might play a role.

The above-mentioned controversy regarding Tᵥ(P) motivated us to study the Verwey transition in magnetite as a function of pressure by far-infrared reflectivity measurements, which comprise both electronic and vibrational properties. The goal of our investigation is not primarily the precise determination of the pressure dependence of the Verwey transition temperature like in other studies, but to characterize the phases of magnetite close to the Verwey transition from an infrared spectroscopic point of view: The overall level of the reflectance spectrum and the phonon mode activation and splitting are considered for various temperatures and pressures. Based on these two criteria, we propose a pressure-temperature phase diagram. We also relate our results to those of earlier works.

II. METHODS

The single crystals of magnetite used in this work were grown from polycrystalline Fe₃O₄ bars by using a floating-zone technique with radiation heating.²⁵ The polycrystalline bars were prepared from α-Fe₂O₃ by the usual ceramic procedures as pressing and sintering in an adapted oxygen atmosphere. The quality of the crystals was checked by electrical transport measurements, showing a sharp increase of the resistivity by a factor of about 100 at the critical temperature Tᵥ ≈ 122 K, which is characteristic for the Verwey transition.²⁶ The low-temperature reflectance measurements under pressure were conducted in the frequency range from

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200 to 700 cm\(^{-1}\) with a frequency resolution 1 cm\(^{-1}\) partly at the infrared beamline of the synchrotron radiation source ANKA and partly in the lab at Augsburg university. A clamp diamond anvil cell (Diacell cryoDAC-Mega) equipped with type IIA diamonds, which are suitable for infrared measurements, was used for the generation of pressures up to 10 GPa. Finely, ground CsI powder was used as quasi-hydrostatic pressure transmitting medium, in order to ensure a well-defined sample-diamond interface throughout the experiment. The pressure in the diamond anvil cell (DAC) was determined \textit{in situ} in the cryostat by the ruby luminescence method.\(^{27}\) The width of the phonon modes in the measured high-pressure reflectance spectra is comparable to that reported earlier on samples at ambient conditions,\(^{3}\) evidencing the quasi-hydrostatic conditions in the DAC.

The reflectance measurements at low temperature and high pressure were carried out using a home-built infrared microscope coupled to the FTIR spectrometer and maintained at the same vacuum conditions, in order to avoid absorption lines of H\(_2\)O and CO\(_2\) molecules. The infrared radiation was focused on the sample by all-reflecting Schwarzschild objectives with a large working distance of about 55 mm and 14\(\times\) magnification. The DAC was mounted in a continuous-flow helium cryostat (Cryo Vac KONTI cryostat). More details about the geometry of the reflectivity measurements can be found in our earlier publications.\(^{28,29}\) As reference, we used the intensity reflected from the CuBe gasket inside the DAC. All reflectance spectra shown in this paper refer to the absolute reflectance at the sample-diamond interface, denoted as \(R_{\text{abs-d}}\). Furthermore, corrections regarding the decaying intensity of the synchrotron radiation with time have been taken into account.

### III. RESULTS AND DISCUSSION

The far-infrared reflectance spectrum of magnetite was measured for several pressures between 0 and 10 GPa as a function of temperature. As an example, we show in Fig. 1(a), the reflectance spectrum at \(\approx 2.5\) GPa for various temperatures. At room temperature, two oxygen phonon modes are observed with frequencies close to 355 cm\(^{-1}\) and 565 cm\(^{-1}\) at low pressure, consistent with earlier reports.\(^{3-5,26,30}\) While cooling down from room temperature to 150 K, which is well above \(T_v,^{17-24}\) the overall reflectance spectrum gradually decreases [see Fig. 1(a)], consistent with a “bad metal” behavior also found in temperature-dependent dc resistivity data.\(^{26}\) Below \(\approx 150\) K, the overall reflectance decreases drastically with a saturation below \(\approx 102\) K. Furthermore, below 150 K, the reflectance spectrum becomes more complex because of the phonon mode splitting and the activation of additional low-frequency phonon modes. By comparing the temperature dependence of the reflectance spectra for two pressures (2.5 and 7.8 GPa), as depicted in Figs. 1(a) and 1(b), it is obvious that this overall evolution of the reflectance spectrum with decreasing temperature is not strongly dependent on the applied pressure. Furthermore, at a fixed temperature, the overall reflectance spectrum is enhanced with increasing pressure, which is consistent with the pressure-induced increase of the conductivity according to dc transport measurements.\(^{17}\)

For a quantitative characterization of the pressure- and temperature-induced changes in the optical response, the reflectance spectra were fitted according to the Fresnel equation for normal-incidence reflectivity taking into account the diamond-sample interface

\[
R_{s-d} = \frac{n_{\text{dia}} - \sqrt{\epsilon_s}}{n_{\text{dia}} + \sqrt{\epsilon_s}}
\]

where \(n_{\text{dia}}\) is the refractive index of diamond and assumed to be independent of pressure and temperature, and \(\epsilon_s\) is the complex dielectric function of the sample. From the function \(\epsilon_s(\omega)\), the real part of the optical conductivity, \(\sigma_{\text{r}}(\omega)\), can be calculated according to Eq. (1), where \(\epsilon_{\text{bg}}\) is the background dielectric constant (here \(\epsilon_{\text{bg}} \approx 1\)). \(\epsilon_s(\omega)\) was assumed to follow the Drude-Lorentz model.\(^{31}\) An example for the fitting is depicted in Fig. 1(a) for \(T = 120\) K at \(P = 7.8\) GPa. To obtain a good fit of the reflectance spectrum, we had to include a Drude term and several Lorentz oscillators describing the phonon modes, while the high-frequency extrapolation was modeled according to ambient-temperature data.\(^{26}\) It is important to note here that the extrapolations are not significant for our conclusions (see below) on the pressure-temperature phase diagram of magnetite. The various excitations (Drude term, phonon modes) at \(T = 120\) K and 7.8 GPa are illustrated in Fig. 2(a) together with the real part of the optical conductivity within the measured frequency range. At the

![Graph](https://example.com/graph.png)
The lowest studied temperature (10 K), the optical conductivity can be described as a sum of Lorentz oscillators reflecting the rich phonon spectrum below $T_v$ [see Fig. 2(b)].

As a criterium for entering the charge-ordered state one can take the saturation of the down-shift of the reflectance spectrum (see Fig. 1) and the absence of a Drude term. Concomitant with the overall lowering of the reflectance spectrum occurs the splitting of the phonon modes and the activation of additional modes. The mode splitting and activation are manifestations of symmetry lowering of the crystal structure (from cubic to monoclinic) at the Verwey transition. Therefore, reaching the maximum number of phonon modes serves as an additional criterium for entering the charge-ordered phase. The temperature-dependent phonon spectrum was characterized based on the Drude-Lorentz fitting, and the extracted mode frequencies are shown in Fig. 3 at 2.5 and 7.8 GPa. Interestingly, the splitting and activation of phonon modes already start at around 150 K, i.e., well above $T_v$, in agreement with earlier infrared studies. Whether or not this is due to the quasi-hydrostatic conditions in the DAC remains an open question, as no systematic study on the pressure dependence

Based on two criteria—the down-shift of the reflectance spectrum and the phonon mode splitting/activation—we can mark the “bad metal” and insulating phases in the pressure-temperature phase diagram of magnetite, as shown in Fig. 4. The most important result is that we do not observe a suppression of the insulating state even at the highest pressure applied (10 GPa), in agreement with some earlier studies. We do not observe the metallization of magnetite above ≈8 GPa and the occurrence of a quantum critical point, as claimed in other works. Whether or not this is due to the quasi-hydrostatic conditions in the DAC remains an open question, as no systematic study on the pressure dependence
of the Verwey transition temperature in the same sample for various pressure transmitting media exists.

IV. CONCLUSION

In conclusion, based on the temperature- and pressure-dependent optical response of magnetite, we find the typical signatures of the Verwey transition, namely (i) the overall lowering of the reflectance related to the entering of the charge-ordered state, and (ii) the splitting and activation of phonon modes due to the lowering of the crystal symmetry. The downshift of the reflectance spectrum and the splitting/activation of phonon modes set a lower bound for $T_v$. Based on these results, we propose a phase diagram for magnetite showing the “bad metal” and the insulating phases. The metallization of magnetite above $\approx 8$ GPa and the occurrence of a quantum critical point is not observed in our data.

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