Small-polaron conductivity in magnetite

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A recent and new theoretical approach for the optical and dc conductivity is applied to magnetite. It is based on a small-polaron (SP) model which takes into account also the polaronic short-range order. The good agreement between the theoretical fit and our new and thorough optical measurements supports the idea of superposition of SP band and hopping conductivity in magnetite.

I. INTRODUCTION

It is well known that magnetite (Fe_3O_4) is a mixed-valence oxide which undergoes a first-order Verwey transition at $T_v \approx 120$ K.[1] However, in spite of many years of research on magnetite, e.g., Refs. 2 and 3, there is no generally accepted explanation either for the Verwey transition or for the electrical conduction mechanism. Of course, an understanding of the electrical transport mechanism depends on the understanding of the exact nature of this transition. In order to bring more light into the as-yet unsolved problem of the Verwey transition and the conduction mechanism, many experiments and theories have been conceived.

Experimentally, the dc conductivity changes abruptly at T_v by a factor of about 100, and above T_v it increases appreciably, reaching a maximum near room temperature.[4] Previous measurements of the optical conductivity at room temperature[2,5] show two sharp peaks at about 0.04 and 0.07 eV which are due to ir-active phonons, a broad maximum near 0.2 eV, and a pronounced broad peak at 0.6 eV which is ascribed to the lowest-energy $3d^6 \rightarrow 3d^5 4s$ transition.[6] Recently, new and thorough investigations[7] reveal the whole phonon spectrum and for the first time also the Drude behavior at low energies.

From the theoretical point of view most of the proposed conduction mechanisms for the $3d^6 \rightarrow 3d^6$ transitions are based on either hopping or band motion of the Fe^{2+} valence electrons (for a discussion see Ref. 8). However, those approaches yield an unsatisfactory description of the electrical conductivity in comparison with the experiment. Recently, a new contribution to the theory was suggested by Ihle and Lorenz.[8]

These authors first emphasize that experimental and theoretical studies have revealed the existence of two types of strong interaction of the valence electrons in Fe_3O_4: the electron-phonon interaction leading to the formation of small polarons (SP's) and the intersite Coulomb interaction resulting in a considerable short-range order (SRO) above T_v. Taking into account the polaronic SRO due to the intersite SP-SP interaction, they developed a microscopic theory of the electrical SP conductivity of Fe_3O_4.

The comparison of this theory with experiments yields good agreement. The dc conductivity can be explained by the superposition of SP band and hopping conduction and the maximum in the optical conductivity near 0.2 eV is proposed to be due to SP hopping. However, a detailed comparison with experiments, especially regarding the optical conductivity, was not performed.

The aim of the present paper is to present a direct correlation between the model of Ihle and Lorenz and our new and thorough optical measurements. First of all we will describe the main features of the theory. We will then present the fitting procedure of the model to our experimental data, followed by the discussion of the obtained results.

II. THEORY

In the theory of Ihle and Lorenz[8] the two basic ingredients are the SP model and the concept of SRO.

The SP system (formed by the spin-down Fe^{2+} valence electrons) is described by the model Hamiltonian

$$H = H_0 - t \sum_{i,j} \phi_{ij} \tilde{c}_i^{\dagger} \tilde{c}_j \ , \tag{1}$$

$$H_0 = -E_b \sum_i \tilde{n}_i + \tfrac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} U_{ij} \tilde{n}_i \tilde{n}_j + \sum_{\mathbf{q},\nu} \omega_{\mathbf{q}\nu} \tilde{b}_{\mathbf{q}\nu}^{\dagger} \tilde{b}_{\mathbf{q}\nu} \ , \tag{2}$$

i,j label the B sites, $\tilde{n}_i = \tilde{c}_i^{\dagger} \tilde{c}_i$, $\tilde{c}_i^{\dagger}$ and $\tilde{b}_{\mathbf{q}\nu}^{\dagger}$ are the creation operators for a SP and a displaced phonon, respectively, and $\omega_{\mathbf{q}\nu}$ is the phonon energy. t is the nearest-neighbor transfer integral, E_b the SP binding energy in the $t=0$ limit, and U_{ij} are the effective SP-SP interaction energies. The operator ϕ_{ij} contains phonon operators up to infinite order. The model is considered in the limit $t \ll E_b$.

The polaronic SRO in the B-site lattice results mainly from the nearest-neighbor SP-SP interaction U_1 and has an essential influence on the thermodynamical and transport properties.[8,9] Let us consider the electrical SP conductivity for $T > T_v$. In the theory the dc conductivity $\sigma_{dc}(T)$ and the real part of the optical conductivity due to the d-d transitions, $\sigma(\omega,T)$, are calculated. In the lowest-order perturbation approach with respect to t, $\sigma(\omega)$ is the sum of the SP band conductivity $\sigma_b(\omega)$ (arising

from SP transitions without changes of the phonon occupation numbers) and the SP hopping conductivity $\sigma_h(\omega)$ (resulting from transitions which are accompanied by multiphonon absorptions and emissions),

$$\sigma(\omega)=\sigma_b(\omega)+\sigma_h(\omega) . \tag{3}$$

The dc conductivity arises from the $\omega\rightarrow 0$ limit of (3), $\sigma_{dc}=\sigma_b+\sigma_h$. For $\omega \ll U_1$ the SP band conductivity results from intraband transitions within three narrow SP subbands separated by U_1,[8] and it obeys the Drude law

$$\sigma_b(\omega)=\frac{\sigma_b}{1+\omega^2\tau_D{}^2} \tag{4}$$

with

$$\sigma_b=e^2\tilde{t}^2\beta y(9+y^4)\tau_{dc}/\sqrt{2}D^2R_1 , \tag{5}$$

$$D=3+4y+y^4,\quad y=\exp(-\beta U_1/2) ,$$

$$\tilde{t}=t\exp(-S_T),\quad S_T=S_0\coth(\beta\omega_0/2) ,$$

$\tilde{t}$ is the polaronic reduced transfer integral, $S_0=0.23E_b/\omega_0$, and $\beta=1/kT$. ω_0 is the mean energy of the highest-frequency ir-active LO mode, $R_1=2.97$ Å is the nearest-neighbor distance, and τ_D, τ_{dc} are mean transport relaxation times. The factor y in (5) describes the thermal activation of the dc band conductivity due to the destruction of SRO with temperature.

The τ_D and τ_{dc} relaxation times are due to the SP-multiphonon scattering and depend on temperature. In general they are different in magnitude (in Ref. 8 the approximation $\tau_D=\tau_{dc}$ was made), since τ_D and τ_{dc} result from the relaxation time $\tau_{k\alpha}$ (α is a subband index) by taking different averages over $\mathbf{k}$ and α.[10] A theoretical estimate of the difference between τ_D and τ_{dc} is not possible. Considering the data for usual semiconductors we expect the ratio τ_D/τ_{dc} to be smaller than about 2.[11] The SP hopping conductivity in the presence of SRO and in the high-temperature region $T>T_0$ ($>T_v$), where

$$kT_0=\omega_0\{2\ln[2S_0+(1+4S_0^2)^{1/2}]\}^{-1} , \tag{6}$$

is given by

$$\sigma_h(\omega)=\sigma_h\frac{A(\omega)}{A(0)}\frac{\sinh(\beta\omega/2)}{\beta\omega/2} \times(1+b_0^2)^{-1/4}\exp[-\omega^2\tau_h^2 r_0(\omega)] \tag{7}$$

and

$$\sigma_h=(2\pi)^{1/2}R_1^{-1}e^2t^2\beta\tau_h A(0)\exp[-2S_0\tanh(\beta\omega_0/4)] , \tag{8}$$

$$\tau_h=[\sinh(\beta\omega_0/2)/S_0]^{1/2}/2\omega_0 ,$$

$$A(\omega)=y\left[9+y^4+\tfrac{3}{2}(3+2y^2)[B_1(\omega)+B_{-1}(\omega)] +3y^2[B_2(\omega)+B_{-2}(\omega)] +\frac{y^4}{2}[B_3(\omega)+B_{-3}(\omega)]\right]\Big/2D^2 ,$$

$$B_n(\omega)=(1+b_0^2)^{1/4}(1+b_n^2)^{-1/4} \times\exp\{-\tau_h^2[(\omega+nU_1)^2r_n(\omega)-\omega^2r_0(\omega)]\} ,$$

$$b_n=2\omega_0\tau_h^2(\omega+nU_1) ,$$

$$r_n(\omega)=2b_n^{-1}\ln[b_n+(1+b_n^2)^{1/2}]-2b_n^{-2}[(1+b_n^2)^{1/2}-1] .$$

The SP conductivity is governed by the model parameters U_1, ω_0, S_0, t, τ_D, and τ_{dc}, where U_1 and ω_0 will be fixed in the fit (Sec. IV). We note that U_1, ω_0, and S_0 satisfy the relation[12]

$$U_1=\frac{4.84}{\epsilon_\infty}\ \text{eV}-6.70S_0\omega_0 , \tag{9}$$

where ϵ_∞ is the high-frequency background dielectric constant. For physically reasonable parameters the dc conductivity below room temperature is dominated by the SP band conduction. With increasing temperature a gradual transition from band conduction to hopping conduction takes place. For the optical conductivity the theory predicts the following behavior: in the far ir region $\sigma(\omega)$ decreases appreciably with frequency which is caused by the Drude law for the SP band conductivity, whereas in the middle-ir region $\sigma(\omega)$ is determined by the SP hopping conductivity which shows a broad maximum between 0.2 and 0.3 eV. A more detailed description of the model will be developed in the next sections.

III. EXPERIMENTS

We have performed optical reflectivity measurements of Fe_3O_4 at 300 and 130 K, between 1 meV and 12 eV using four spectrometers.[7] We have used best-quality natural single crystals, polished and annealed for 24 h at 720 °C. All optical properties, such as, e.g., the real part of the optical conductivity $\sigma_1(\omega)$, can be obtained through a Kramers-Kronig transformation of the reflectivity data.[13]

For the extrapolation towards $\omega\rightarrow 0$ we have made use of the Hagen-Rubens relation (see Sec. IV), obtaining through the Kramers-Kronig (KK) transformation a rather good compatibility between $\sigma_1^{KK}(\omega)$ for $\omega\rightarrow 0$ and σ_{dc}^{expt}. The main features in these optical spectra are the following: first of all, the observation of a Drude contribution at low energies even though it is only a small effect at 130 K, and second, a structure at 0.25 eV, which exhibits a small shift towards higher energy as the temperature decreases.

Regarding this last structure $\sigma_1(\omega)$ is in addition superimposed on another peak, centered at ≈ 0.62 eV. The latter is identified with the lowest-energy $3d^6\rightarrow 3d^5 4s$ transition ($^6A_{1g}$).[6] Finally, we have measured $\sigma_{dc}(T)$, between 150 and 450 K, on the same crystal sample, using the van der Pauw method.[14] Our experimental data agree with other measurements, as, e.g., those by Miles *et al.*,[4] even though our broad maximum at ≈ 350 K is not so pronounced.

However, the above method is, especially for magnetite, not very suitable for measurements below T_v. In any case

we are interested in the temperature range above T_v and our experimental data can constitute, from this point of view, a good starting point for our discussion.

IV. FIT PROCEDURE AND RESULTS

The real part of the total optical conductivity, $\sigma_1(\omega)$, is the sum of the contributions due to the d-d transitions [$\sigma(\omega)$ in Sec. II], the ir-active TO phonons (described by oscillators), and the d-s transition. Since for this transition there is no microscopic information, for simplicity we describe it phenomenologically also as an oscillator. Thus, we have

$$\sigma_1(\omega)=\sigma(\omega)+\epsilon_0\sum_j f_j\gamma_j\omega^2[(\varepsilon_j^2-\omega^2)^2+\gamma_j^2\omega^2]^{-1}\,, \qquad (10)$$

where j labels the phonons and the d-s oscillator ε_j, γ_j, and f_j are the energy, damping, and oscillator strength of the jth oscillator, respectively.

We have fitted $\sigma_1(\omega)$ at 300 and 130 K within the model of Ihle and Lorenz using formulas (3), (4), (7), (8), and (10). In our fit procedure the parameters U_1 and ω_0 are fixed *ab initio*. U_1 is determined by the comparison of the theoretical dc conductivity below T_v with experiments which yields $U_1=0.11$ eV.[8] ω_0 is taken as the frequency of the highest ir-active LO mode which is derived from the energy-loss spectrum obtained from our reflectivity data by a KK transformation. We obtain $\omega_0=0.0765$ eV.

Let us consider the fit at 300 K. First we have calculated the theoretical $\sigma_1(\omega)$ in the energy range between 0.08 and 0.65 eV as a superposition of the SP hopping contribution and the d-s oscillator [in this energy range the band term $\sigma_b(\omega)$ is negligible]. The fitted parameters are S_0, t for $\sigma_h(\omega)$, and ε, γ, and f for the d-s transition. The obtained parameters S_0 and t are henceforth fixed in our fit. Then, as a second step, we have considered the low-energy range between 0.001 and 0.08 eV. Here $\sigma_1(\omega)$ is the sum of four oscillators, representing the four ir-

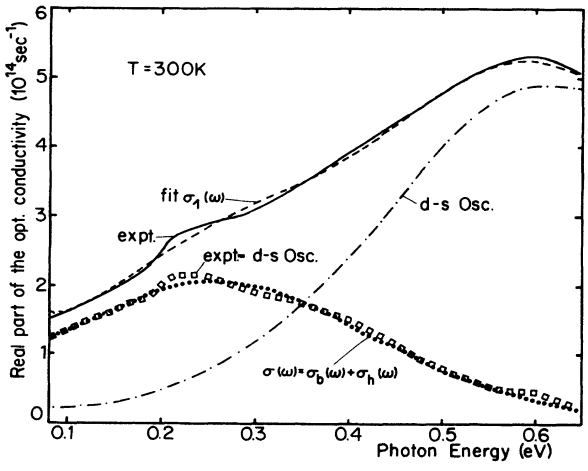

FIG. 1. Real part of the optical conductivity of Fe_3O_4 at 300 K between 0.08 and 0.65 eV, with the theoretical fit, explained in the text.

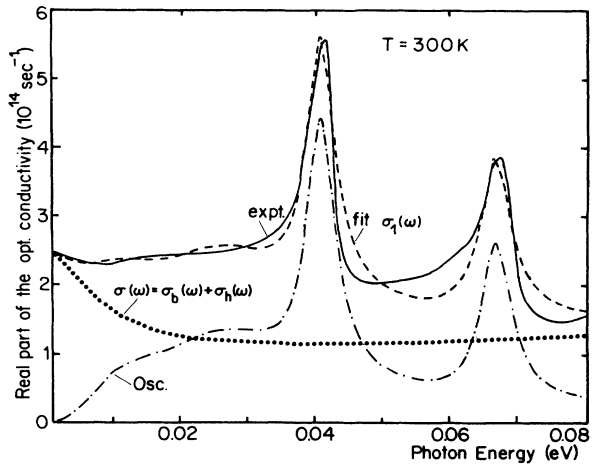

FIG. 2. Real part of the optical conductivity of Fe_3O_4 at 300 K up to 0.08 eV, with the theoretical fit, explained in the text.

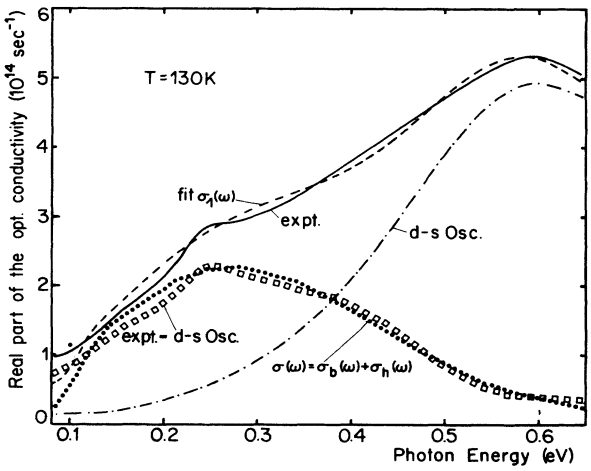

FIG. 3. Real part of the optical conductivity of Fe_3O_4 at 130 K between 0.08 and 0.65 eV, with the theoretical fit, explained in the text.

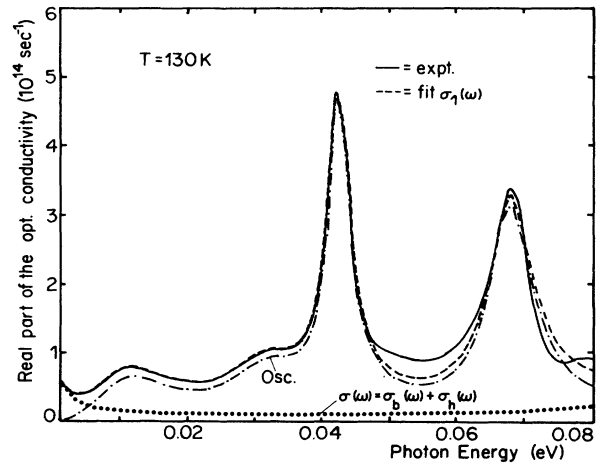

FIG. 4. Real part of the optical conductivity of Fe_3O_4 at 130 K up to 0.8 eV, with the theoretical fit, explained in the text.

TABLE I. Parameters for the four ir-active phonon and d-s oscillators and for the model parameters S_0, t and τ_D at 300 K. $S_0=1.79$, $t=0.0546$ eV, $\tau_D(300\text{ K})=0.8\times10^{-13}$ s.

	Osc. I	Osc. II	Osc. III	Osc. IV	d-s osc.
ε (eV)	0.0123	0.0277	0.0410	0.067	0.615
γ (eV)	0.0172	0.0269	0.005	0.0055	0.538
f (eV^2)	0.00912	0.0230	0.0153	0.0104	2.19

active phonon modes, and of the band and hopping contribution. The hopping term in this energy range has fairly constant behavior and the band contribution takes the main importance for the fit. In fact, we fitted the parameters of the four phonon oscillators and τ_D in (4). Thereby, the value of σ_b in (4) is set equal to $\sigma_b=\sigma_{dc}^{expt}-\sigma_h=14\times10^{13}$ s^{-1},[15] since σ_h is equal to 1×10^{14} s^{-1} (for t and S_0 fitted before).

From the experimental point of view we do not observe the two lowest-energy phonons at 300 K. These are, however, introduced into the fit and we justify this procedure by the experimental data at 130 K, where the four ir-active modes are clearly detected.[7]

Figures 1 and 2 represent the results of the fit and in Table I we summarized the fit parameters. We have also performed a fit of $\sigma_1(\omega)$ in the whole energy range, which yields only very small changes in the parameters, giving a good justification of the above procedure.

Next we consider the fit at 130 K using the S_0 and t values of Table I, even though our reference temperature T_0 is equal to 223 K (6), below which a certain ambiguity about the applicability of the theory arises. Figure 3 shows the fit between 0.08 and 0.65 eV, obtained by adjusting the d-s oscillator to the hopping contribution (Table II). Between 0.08 and 0.2 eV the fit is only approximately good and $\sigma_1(\omega)$ is a little higher than the experimental curve. Attention must be paid to the fact that in this energy range the optical conductivity $\sigma_1(\omega)$ is very sensitive to the matching of the different spectrometers. In fact, at 0.08 eV we change the spectrometers in our measurement, and a small uncertainity can therefore occur.

Figure 4 shows the low-energy part of the fit, where the parameters of the four phonon modes and τ_D have been fitted again (Table II). In this energy range the hopping term is very weak. The small band contribution (4) is fitted, setting $\sigma_b=6\times10^{13}$ s^{-1}, since $\sigma_h=1\times10^{13}$ s^{-1} and for σ_{dc}^{expt} we have taken 7×10^{13} s^{-1}.[15]

V. DISCUSSION

Figures 1–4 demonstrate a fair agreement between experiment and theoretical fit. Particularly in Fig. 1, we note that the hopping contribution agrees very well with the difference between the experiment and the d-s oscillator.

The maximum in $\sigma(\omega)$ for 300 K appears at $\omega_m=0.26$ eV where $\sigma(\omega_m)=2.1\times10^{14}$ s^{-1}, whereas for 130 K we obtain $\omega_m=0.28$ eV and $\sigma(\omega_m)=2.3\times10^{14}$ s^{-1}. The maximum frequencies are a little bit higher than the experimental values. The slight increase of ω_m and $\sigma(\omega_m)$ with decreasing temperature, observed in our experiments, is in agreement with the predictions of the theory[8] which supports the explanation of the optical conductivity maximum near 0.25 eV by SP hopping.

From U_1, ω_0, and S_0, by relation (9) we calculate $\epsilon_\infty=4.73$, which is a realistic value and is consistent with the value given by Samokhvalov *et al.*[16]

In the low-energy range our fit clearly demonstrates the existence of SP band conduction in Fe_3O_4 described by the Drude law. For the Drude relaxation time τ_D we obtain $\tau_D(300\text{ K})=8\times10^{-14}$ s and $\tau_D(130\text{ K})=3.06\times10^{-13}$ s, which shows a physically reasonable temperature dependence of τ_D. Thus the fit at different temperatures proves the consistency in our model.

Let us now discuss the dc conductivity. First we consider the temperature dependence of τ_{dc}. Since we have not performed a microscopic calculation of τ_{dc}, we calculate it by imposing $\sigma_{dc}^{expt}(T)=\sigma_{dc}^{theor}(T)=\sigma_b(T)+\sigma_h(T)$. By (5) and (8) we get

$$\tau_{dc}(T)=\frac{\sigma_{dc}^{expt}-\sigma_h}{\tilde{\alpha}}\ , \tag{11}$$

where $\tilde{\alpha}=e^2\tilde{t}^2\beta y(9+y^4)/\sqrt{2}D^2R_1$.

Of course, σ_h and $\tilde{\alpha}$ are calculated with the fitted parameters t and S_0 of Table I. For $T=300$ and 130 K we obtain $\tau_{dc}=8.7\times10^{-14}$ s and $\tau_{dc}=1.4\times10^{-13}$ s, respec-

TABLE II. Parameters for the four ir-active phonon and d-s oscillators and τ_D at 130 K. $\tau_D(130\text{ K})=3.06\times10^{-13}$ s.

	Osc. I	Osc. II	Osc. III	Osc. IV	d-s osc.
ε (eV)	0.0115	0.0315	0.0425	0.068	0.601
γ (eV)	0.0141	0.0141	0.0041	0.0079	0.430
f (eV^2)	0.00726	0.00745	0.0153	0.0194	1.79

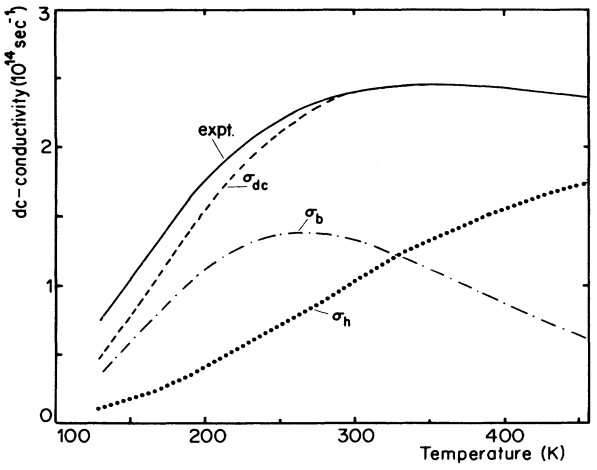

FIG. 5. Experimental and theoretical dc conductivity of Fe_3O_4 above T_v, with the band and hopping contributions.

tively. For all other temperatures in the range between 150 and 450 K, where we have measured $\sigma_{dc}(T)$ on our single-crystal sample, we obtain a dc relaxation time that strongly decreases with increasing temperature for $T_v < T < 250$ K, whereas for $250 < T < 350$ K τ_{dc} decreases only slightly.

From our experimental data on $\sigma_{dc}(T)$ for temperatures $T > 350$ K we obtain somewhat increased values of τ_{dc}. This can be explained by the error in the measurements of σ_{dc}; we have just noticed that our maximum is not so pronounced as in Miles *et al.*[4] and at high temperatures an error of about 10% can easily occur in our method.

Considering the ratio $\tilde{\gamma} = \tau_D / \tau_{dc}$, we obtain $\tilde{\gamma}(300\ \text{K}) = 0.92$ and $\gamma(130\ \text{K}) = 2.18$ which are reasonable values (see Sec. II). In order to illustrate the superposition of SP band and hopping conduction in the dc conductivity and the temperature dependence of τ_{dc} we calculate $\sigma_{dc}(T)$ within the model by (5) and (8) using the parameters of Table I and $\tau_{dc}(300\ \text{K})$ given above. Figure 5 also represents the theoretical curve compared with the experimental data. At high temperatures there is good agreement between theory and experiment. For temperatures $T_v < T < 250$ K the differences confirm the qualitative temperature dependence of τ_{dc} as described before. Figure 5 also demonstrates the consistency between $\sigma_1(\omega)$ and $\sigma_{dc}(T)$ and supports again the idea of the superposition of a band and a hopping contribution in $\sigma_1(\omega, T)$. We note that our results show that the SP hopping theory for $T > T_0 = 223$ K also holds rather well for 130 K.

Concerning the phonon parameters, summarized in Table II, we first note, that they are only slightly different from the ones fitted in a recent publication,[7] where, however, the hopping term was totally neglected and the band contribution was expressed in terms of the plasma frequency and where a σ_{dc} of 4×10^{13} s^{-1} (Ref. 1) was used for the Hagen-Rubens extrapolation. Comparing the values of these parameters at 300 and 130 K (Tables I and II), we note that the phonon energies ε_i fulfill the correct relations resulting from the mode Grüneisen parameters, namely $d\varepsilon_i/dT < 0$. The damping parameters also generally satisfy the physically reasonable relations $d\gamma_i/dT > 0$.

Regarding the *d-s* transition peak at 0.6 eV, one can explain the temperature dependence of its width ($d\gamma/dT > 0$) primarily by the electron-phonon scattering which smears out the absorption edge.

VI. CONCLUSION

By our new experimental and theoretical studies we have reached a clear and consistent physical picture of the optical and dc conductivity of Fe_3O_4. The essential new result of this work is that the optical conductivity due to *d-d* transitions can now be explained by the superposition of SP band and hopping conductivity. All our results give strong evidence that the relevant physical mechanisms for electrical conduction in Fe_3O_4 are incorporated in the model by Ihle and Lorenz. We note that the basic concepts of that model (SRO of SP) also seem to be supported by the recent results of muon-spin-relaxation (μSR) experiments by Boekema *et al.*[17]

Using for our fit procedure of the experimental data the SP model, based on a small set of parameters $(t, S_0, \tau_{dc}, \tau_D)$, with only the relaxation times τ_{dc} and τ_D being temperature dependent, and including the phonon and *d-s* transition structures, the model is found to be consistent with the dc and the optical conductivity even at different temperatures. It must be noted that, with exception of U_1 determined *ab initio* from the literature, all other parameters in the model are fitted from or determined by measurements always carried out on the same sample. An extension of the measurements of $\sigma_{dc}(T)$ for $T < T_v$ would be useful for complete consistency.

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