Optical properties of $YBa_2Cu_3O_{7-\delta}$ thin films

Y. Yagil
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

F. Baudenbacher
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom and Fakultät für Physik, E10, Technische Universität München, D-8046 Garching, Federal Republic of Germany

M. Zhang
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom and Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom

J. R. Birch
National Physical Laboratory, Queens Road, Teddington, Middlesex TW11 0LW, United Kingdom

H. Kinder
Fakultät für Physik, E10, Technische Universität München, D-8046 Garching, Federal Republic of Germany

E. K. H. Salje
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom and Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom

(Received 27 February 1995; revised manuscript received 31 May 1995)

Temperature-dependent reflectance and transmittance measurements (1250–8000 cm^{-1}) of thin Y-Ba-Cu-O films are reported and the complex dielectric response $\varepsilon(\omega)$ is directly determined from the measured data. We find that $\varepsilon(\omega)$ is more complex than predicted by any of the existing models, in particular the marginal and the nested Fermi liquids, as well as the two-component approach (Drude and midinfrared terms). A phenomenological analysis reveals either a two-fluid or a complicated one-fluid model, which is yet to be explained theoretically. The near-infrared (NIR) transmittance is weakly temperature dependent in the normal state, but almost temperature independent in the superconducting state. Both the normal and the superconducting states are anomalous and non-Fermi-liquid-like with renormalization of energies much higher than any superconducting energy gap. Such observations have previously been reported only in powder absorbance measurements but not in single-crystal and thick-film reflectance data. We present a quantitative analysis in which the powder absorbance results are recovered from thin-film data. The NIR response is argued to be of crucial importance for the understanding of the high-temperature superconductors in both the normal and the superconducting states.

INTRODUCTION

The optical properties of high-temperature superconductors (HTSC) in the normal and the superconducting states are still not understood, and some controversies are yet to be resolved.[1] It is generally believed that superconductivity occurs primarily in the Cu-O planes and that the Cu-O chains, when existing, are less crucial. The optical conductivity in the mid- and near-infrared regimes (MIR, NIR) indicates non-Drude behavior: if a Drude model is assumed then an extremely short mean free path should be used to fit the optical data, and the temperature dependence is much weaker than expected due to the dc conductivity. Several indications show that the MIR band is due to the Cu-O planes, for example the doubling of the oscillator strength when the number of planes is doubled, observed in 2201 and 2212 Bi-Sr-Cu-O.[2] Near-infrared powder absorbance measurements of pure and doped Y-Ba-Cu-O,[3] Bi-Sr-Cu-O 2212,[4] and La-Sr-Cu-O (Ref. 5) reveal a remarkable temperature dependence above and below the superconducting transition temperature T_c: the integrated absorbance (typically 4000–8000 cm^{-1}) increases upon cooling up to T_c where a sharp slope change is observed. At lower temperatures the integrated absorbance saturates and even decreases. Such behavior cannot be explained within a normal Fermi-liquid approach since $\omega \sim 0.5-1$ eV$\gg 2\Delta$ where Δ is some superconducting energy gap ($\sim$25 meV for Y-Ba-Cu-O). The weak temperature dependence in the normal state, which is

not correlated to the temperature dependence of the dc resistance, and the observation of the superconducting transition in NIR frequencies, are thus one of the crucial issues in the understanding of these materials. Nevertheless the temperature dependence of the NIR response have attracted little attention till now, mainly because the weaker temperature dependence below T_c has not been reported in single-crystal and thick-film reflectance measurements, considered as more reliable probes compared to powder absorbance measurements. It is the aim of this work to (a) explore the exact NIR response of Y-Ba-Cu-O and (b) to resolve the discrepancies between absorbance and reflectance data.

Optical properties of solids are most commonly measured by optical reflectance of bulk, single-crystal, and thick-film samples followed by Kramers-Kronig (KK) analysis. While this technique is usually both reliable and powerful, it suffers from three main drawbacks: (a) the KK analysis requires extrapolations to zero and infinite frequencies, the effect of which is not always negligible; (b) it is hard to detect weak temperature dependence in reflectance measurements due to the limited accuracy of the experimental method, while such variations might reflect stronger changes in the optical constants; (c) reflectance measurements require high-quality samples with optically smooth surface, therefore it is difficult to conduct doping-dependent measurements or to analyze new compounds. Another experimental method is powder absorbance measurements where sample preparation is much easier, however a quantitative analysis is quite difficult and even ambiguous. A third method is to measure directly the *reflectance and transmittance* of thin films and calculate the dielectric response at each frequency without further assumptions. In this case the film thickness can be selected so that both reflectance and transmittance of the same film would be experimentally accessible thus reducing the experimental uncertainties. However, preparation of suitable thin films is not trivial, and there are further complications and limitations due to the optical response of the substrate. Since each method has advantages and disadvantages, one should combine them in order to explore the full picture. In this work we use the less common thin-film technique to study the optical response of Y-Ba-Cu-O and its temperature dependence. Comparison with published reflectance and absorbance data achieves a consistent description of the dielectric response in the MIR and NIR regimes which is more complex than that found by reflectance measurements. We also show that earlier absorbance data can be understood by an effective-medium approach enabling quantitative analysis of such measurements.

EXPERIMENTAL

Y-Ba-Cu-O films were deposited on high-quality both-sides-polished MgO substrates by thermal coevaporation at substrate temperature of 650 °C and oxygen pressure of 10^{-3} mbar near the sample surface. After growth the oxygen pressure was increased to 50 mbar and the sample cooled to room temperature within 20 min. The substrate quality and the growth were monitored with reflection high-energy electron diffraction *in situ*.[6]

Reflectance $\mathscr{R}$ and transmittance $\mathscr{T}$ measurements have been conducted on several Y-Ba-Cu-O films using a Bruker 113V Fourier transform spectrometer equipped with a constant flow helium cryostat. The sample holders are designed to enable alternate sample and reference measurements (for both $\mathscr{R}$ and $\mathscr{T}$), eliminating instabilities of the spectrometer. For the reflectance data thick Al or Au mirrors have been used as references, while the transmittance measurements were done relative to a clean MgO substrate. Each spectrum is an average of 250–500 scans. Reflectance data have been measured from 150 to 8000 cm^{-1} using three different setups [far-infrared (FIR), MIR, and NIR], and the transmittance data were recorded at 700–8000 cm^{-1} (MIR and NIR regimes). Since MgO has strong phonon absorption bands below 1250 cm^{-1}, observed in both reflectance and transmittance spectra, we limit our discussion to higher frequencies. Weak temperature dependence in both $\mathscr{R}$ and $\mathscr{T}$ were verified by repeated measurements and by exchanging the sample and the reference positions. Finally the complex dielectric response was directly calculated form the measured data at each frequency, including multiple reflectance inside the film and the substrate. The calculated dielectric response is therefore more accurate than that obtained by reflectance measurements followed with Kramers-Kronig analysis where extrapolation to zero and infinite frequencies are needed.

RESULTS

The dc resistivity $\rho(T)$ of a 800 Å Y-Ba-Cu-O film is shown in Fig. 1. The onset of superconductivity occurs at 88 K, and zero resistance at 85.5 K. The dc resistivity of a 600 Å film is similar, with onset at 84.5 K and zero resistance at 82.5 K. The data suggest high-quality thin films with rather low resistivity (140 $\mu\Omega$ cm at 100 K), linear temperature dependence where $\rho(295\text{ K})/\rho(100\text{ K})=2.85$, and nearly zero intercept of the extrapolated $\rho(T)$ curves. The films thicknesses were accurately measured by microprobe analysis,[7] which also revealed excess yttrium but otherwise close to ideal stoichiometry and fully oxygenated composition within experimental uncertainties. The excess yttrium is believed to form very small yttria (Y_2O_3) particles, not observed in the x-ray measurements. The x-ray-diffraction pattern in both 2θ and rocking scans of the {004}, {005}, {007}, {108}, {1010}, and {2011} Bragg peaks show no orthorhombic splitting, suggesting that the films have a tetragonal tweed microstructure rather than are twinned orthorhombic material,[8] therefore there is a high degree of disorder in the Cu-O chain planes. This might be the reason for the slightly reduced T_c, however further study is needed to draw definite conclusions on this subject.

The measured reflectance and transmittance of an 800 Å Y-Ba-Cu-O film at 95 K and its optical conductivity $\sigma(\omega)$ calculated from the measured data are shown in Figs. 2 and 3. The optical reflectance is consistent with that measured on other films, prepared by laser ablation or sputtering. We have found large variations of the transmittance for different films (in particular films thicker than 1000–1500 Å), where generally the transmittance is higher and the frequency dependence weaker compared with the data in Fig. 2. Scanning electron microscopy analysis of such films have shown that their transmittance is controlled by pinholes and microcracks, which indeed vary from film to film and between different preparation techniques. The sensitivity of the opti-

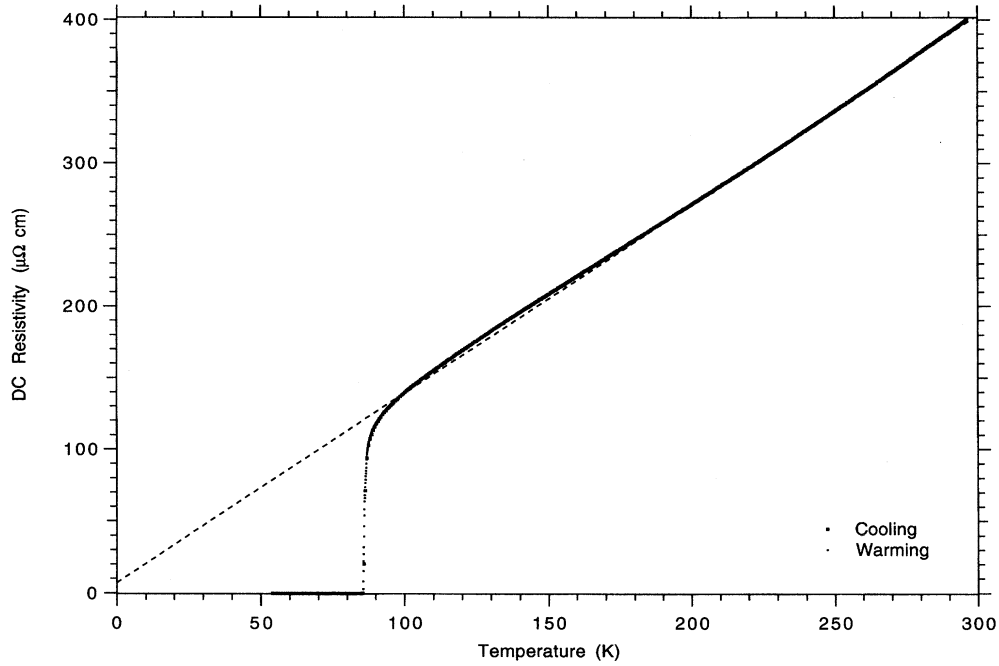

FIG. 1. Temperature dependence of the dc resistivity of 800 Å Y-Ba-Cu-O film. Dashed line shows the extrapolated close to zero intercept of the high-temperature resistivity.

cal transmittance to inhomogeneities is also consistent with recent theoretical predictions for inhomogeneous metal films in the limit of strong skin effect.[9] In contrast films prepared by thermal coevaporation with close stochiometric control are segregation free. Scanning tunneling microscopy measurements reveal a residual roughness of 5–8 monolayers (6–10 nm) due to the screw dislocation mediated growth.[6]

The weak frequency dependence at 3000–7000 cm^{-1} (Fig. 3) is consistent with the *a-axis* optical conductivity of untwinned single crystals[10,11] suggesting that in the above spectral range the Cu-O chains contribution is negligible, i.e., *the optical conductivity of the Cu-O planes is directly measured.* This result is a further indication for the high degree of disorder in the Cu-O chains observed in the x-ray

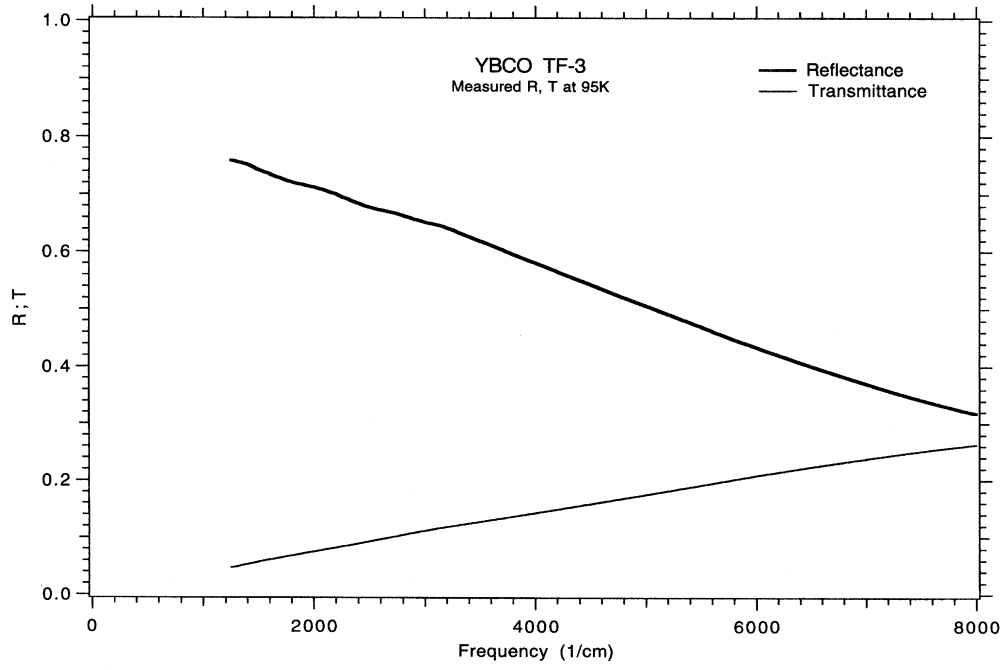

FIG. 2. Measured reflectance and transmittance of an 800 Å Y-Ba-Cu-O film on MgO substrate at 95 K.

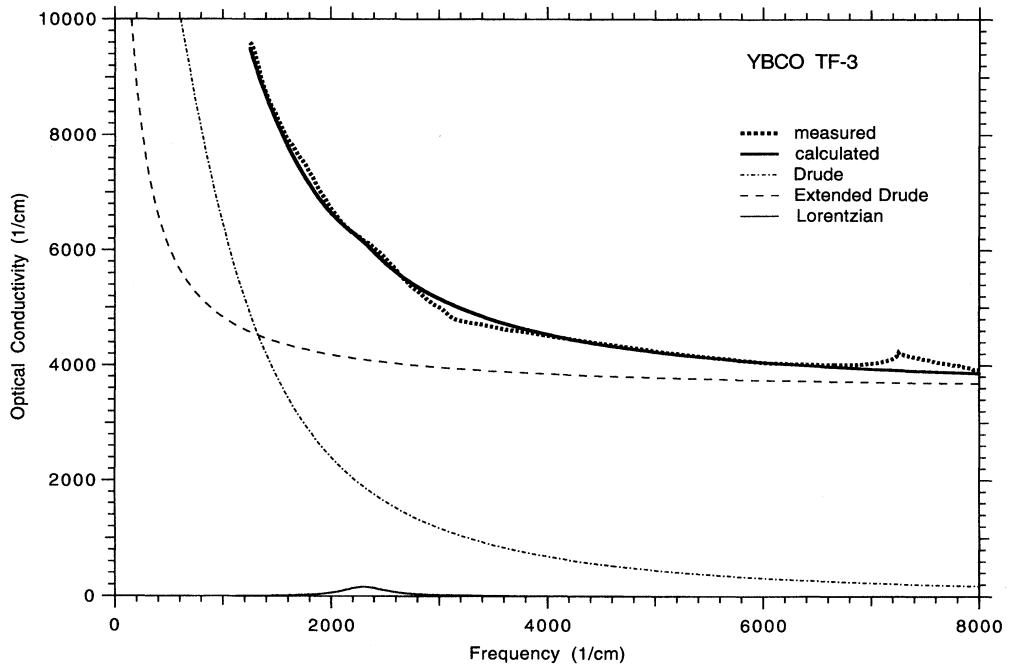

FIG. 3. The optical conductivity calculated from the data in Fig. 2 (dots) and the fitted optical conductivity (see text). The dip and peak at 3000 and 7000 cm^{-1}, respectively, are due to experimental artefacts.

data. We note, however, that one should expect appreciable contribution of the chain segments at higher frequencies. Since both $\mathscr{R}$ and $\mathscr{T}$ are measured, the (complex) dielectric response at each frequency is independently calculated, allowing a detailed comparison with theoretical predictions. *Similar measurements on a 600 Å film revealed the same results:* the optical constants calculated from the measured $\mathscr{R}$, $\mathscr{T}$ are similar to those calculated from the 800 Å film data. Figure 4 shows the measured dielectric response of the 800 Å film at 95 K obtained from the measured $\mathscr{R}$, $\mathscr{T}$. We have tried to fit the experimental data with several expressions for the (complex) dielectric response, including the marginal[12] and the nested[13] Fermi liquids as well as a simple Drude plus a few oscillators (see review in Ref. 1). However, within the limits of physical parameters that are in general agreement with published data, none of these fit both real and imaginary parts of the dielectric response even when additional oscillator profiles are added, i.e., when the number of free parameters is rather large. In particular, the real part of the dielectric response in the NIR regime cannot be fitted by a wide oscillator, referred to as the MIR band in some publications. It is important to note here that the *optical conductivity* $\sigma(\omega)=(\omega/4\pi)\mathrm{Im}\varepsilon$ might well be fitted by any of the above models *over the measured frequency regime* [such fitting, however, does not agree with the real part of $\varepsilon(\omega)$ as discussed above]. This is another manifestation of the importance of extrapolations to zero and infinite frequencies: only when $\sigma(\omega)$ is known at *all frequencies* there is no additional information in the real part of $\varepsilon(\omega)$.

We use a purely phenomenological approach to model the measured (complex) dielectric response function (Fig. 4). The weak frequency dependence at 3000–7000 cm^{-1} is well analyzed by an extended Drude model were the scattering rate Γ^* and the square plasma frequency ω_p^{*2}

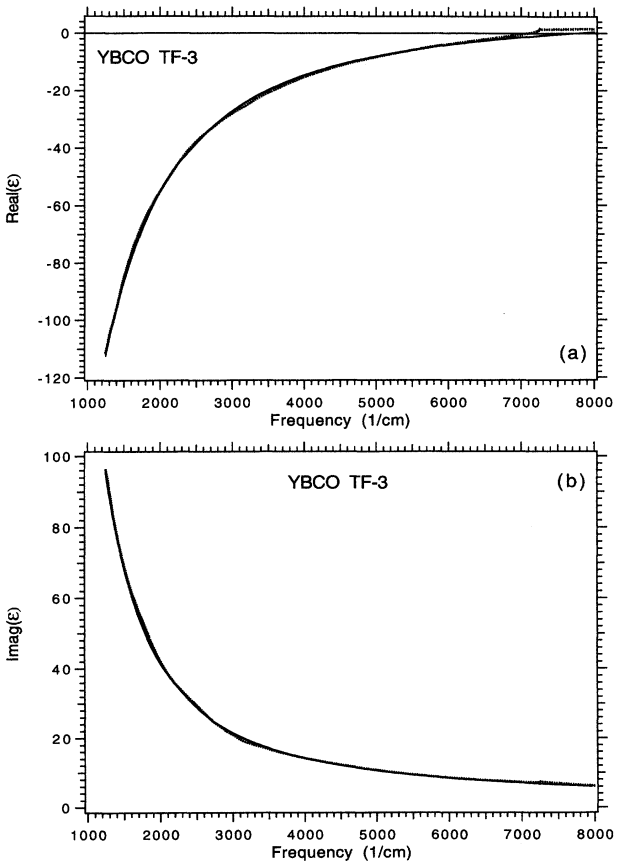

FIG. 4. Measured (dots) and fitted (full line) dielectric function at 95 K, see text for details. (a) real part, (b) imaginary part.

TABLE I. The parameters used to fit the measured dielectric response at 95, 150, and 250 K.

Temperature (K)	95	150	250
ϵ_∞	10.5	10.5	10.5
ω_{pD} (cm^{-1})	12 800	13 300	14 200
Γ_D (cm^{-1})	880	910	950
ω_{ED0} (cm^{-1})	5 500	5 000	4 100
ω_{ED1} (cm^{-1})	92 000	89 000	85 000
Γ_{ED0} (cm^{-1})	150	320	600
g_Γ	0.75	0.75	0.75
ω_{be} (cm^{-1})	1 000	1 150	1 500
ω_e (cm^{-1})	2 300	1 100	500
Γ_e (cm^{-1})	500	530	600
ρ_{dc}(opt) ($\mu\Omega$ cm)	155	220	250
ρ_{dc}(meas) ($\mu\Omega$ cm)	140	210	335

$=4\pi n^* e^2/m^*$ depend linearly on frequency. At lower energies the measured optical conductivity increases more rapidly with decreasing frequency, which might be fitted by an additional (simple) Drude term (see Fig. 3). Finally, better fitting to the real part of the dielectric response at low frequencies is obtained by adding a weak oscillator at low frequency. This model yields the following complex dielectric response (see Table I for parameters values):

$$\tilde{\varepsilon}(\omega)=\varepsilon_\infty+\varepsilon_D+\varepsilon_{\mathrm{ED}}+\varepsilon_{be}, \tag{1}$$

where the "normal Drude" terms is

$$\varepsilon_D=-\frac{\omega_{pD}^2}{\omega^2+\Gamma_{D^2}}+i\frac{\omega_{pD}^2\Gamma_D}{\omega(\omega^2+\Gamma_{D^2})}, \qquad \omega_{pD}^2=\frac{4\pi ne^2}{m}. \tag{2}$$

The extended Drude part has the following form in the relevant frequency range:

$$\varepsilon_{\mathrm{ED}}=-\frac{\omega_p^{*2}}{\omega^2+\Gamma^{*2}}+i\frac{\omega_p^{*2}\Gamma^*}{\omega(\omega^2+\Gamma^{*2})}, \qquad \omega_p^{*2}=\omega_{\mathrm{ED0}}^2+\omega_{\mathrm{ED1}}|\omega|, \qquad \Gamma^*=\Gamma_{\mathrm{ED0}}+g_\Gamma|\omega|, \tag{3}$$

and the oscillator is described by a Lorentz dielectric function of bound charge carriers:[1]

$$\varepsilon_{be}=\frac{\omega_{be}^2}{\omega_e^2-\omega^2-i\omega\Gamma_e}. \tag{4}$$

The above phenomenology is quite arbitrary in so far as it uses traditional response functions. Its advantage is that it provides simple physical insight and reasonable consistency with published data. The main, but not the only, contribution in the NIR regime is that of the "extended Drude" (ED) fluid, which is in agreement with both the marginal and the nested Fermi-liquid models.[12,13] This part of the phenomenological dielectric function is also consistent with published data obtained by KK analysis of reflectance measurements.[1] In Fig. 3 the distribution of oscillator strength between the two fluids is shown. The ED fluid dominates at high frequencies, while the normal Drude component has comparable strength at lower frequencies. Since the experimental data are limited to $\omega>1250$ cm^{-1} the accuracy of the distribution of oscillator strength at low frequencies is somewhat limited.

Before we discuss our results further, we comment on the reliability of data obtained by reflectance measurements followed by Kramers-Kronig analysis and of our data. Firstly, it is worthwhile to remember that the KK analysis is very sensitive to extrapolation to high frequencies when the reflectance data are smooth over the measured frequency range as is the case in Fig. 2. The phase of the reflected light is obtained by the following expression:

$$\theta(\omega)=\frac{\omega}{\pi}\int_0^\infty\frac{\ln\mathscr{R}(\omega')-\ln\mathscr{R}(\omega)}{\omega^2-\omega'^2}\,d\omega', \tag{5}$$

which rapidly decreases as ω' deviates from ω. However, if $\mathscr{R}(\omega)\approx\mathscr{R}(\omega')$ the contribution of high frequencies can be quite significant. Model calculations, based on the measured spectra, show that $\theta(\omega)$ at say 5000 cm^{-1} has comparable contributions from "measured" (0–10 000 cm^{-1}) and extrapolated data. Typically, the extrapolation to high frequencies is based on published data matched to the experimental results. Yet the dielectric response obtained by reflectance and transmittance measurements is far more reliable than that obtained by KK analysis of reflectance data.

The second major problem is that in reflectance measurements the absolute value of the measured reflectance has an uncertainty of some 2–3%. The optical transmittance is more accurate (better than 1%). We have thus repeated the calculation of the dielectric response for different calibrations of the reflectance data. For example a vertical shift of 3% in the measured reflectance ($\mathscr{R}=\mathscr{R}_{\mathrm{meas}}+0.03$) causes a reduction of 12% in both $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, namely the plasma frequencies in the above model are changed by less than 10%. The spectral dependence is only weakly affected by the absolute calibration, hence the experimental uncertainties do not alter our conclusions.

We now turn to the temperature dependence in the normal state. Both reflectance and transmittance are weakly temperature dependent in the measured frequency regime, with typical variations of ~1%. The accuracy of the measurement is of the same order, hence small variations had to be confirmed by repeated measurements. In the transmittance data we find a vertical shift of the spectrum due to temperature without a noticeable change in slope. These variations are beyond the experimental uncertainties. For the reflectance we find larger variations as well as slope changes at frequencies below 2000 cm^{-1}. At higher energies there is no slope change and the experimental data suggest a weak temperature dependence in the normal state, where at room temperature the reflectance is 1% lower than at 95 K. However, these variations are within the reproducibility of the spectra; hence from our measurements we cannot distinguish between temperature independent and weak temperature dependence. Single-crystal measurements by Schlesinger *et al.*[14] revealed that the reflectance at 105 K is some 2% higher than at 250 K throughout the relevant spectral range. Based on Ref. 14, we consider the NIR reflectance to be temperature dependent

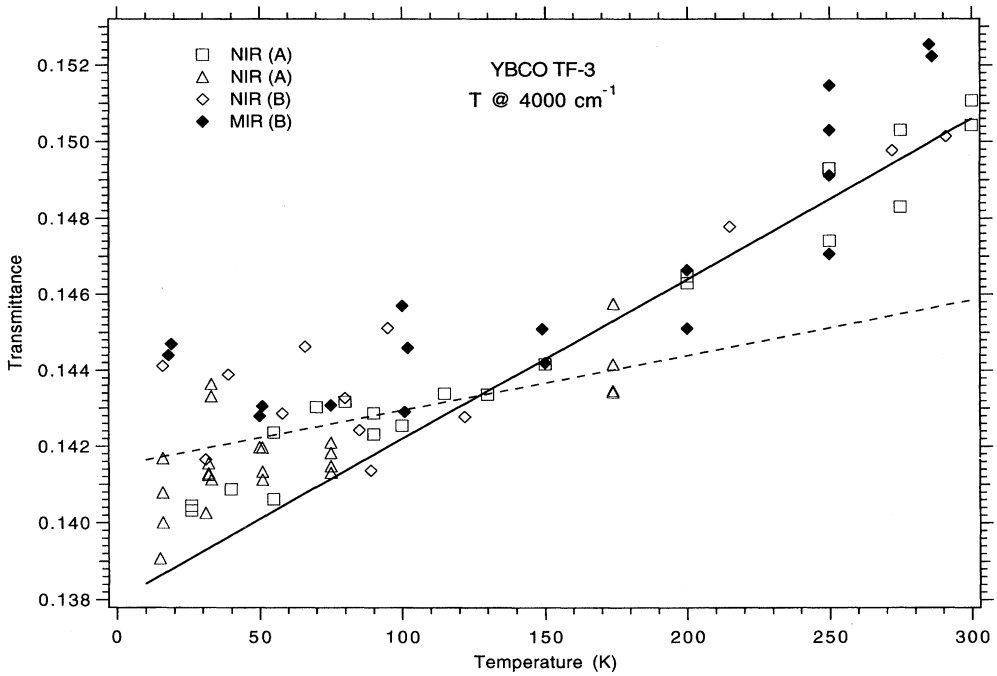

FIG. 5. Temperature dependence of the optical transmittance at 4000 cm^{-1}. Note that the vertical scale is largely magnified: 1.5%. The data show repeated measurements using NIR and MIR spectrometer arrangements. The NIR data are measured in two configurations *A* and *B* in which the sample and the reference positions have been exchanged. The lines are guides to the eye. Note the slope change near the superconducting transition temperature T_c.

and analyze the data accordingly. To avoid extra uncertainty in the calculated dielectric functions due to the limited reproducibility of the reflectance spectra, we use the 95 K NIR reflectance for all temperatures. For $T>95$ K the spectra are vertically shifted according to the above temperature dependence. Therefore the 150 and 250 K are downshifted by 0.3 and 0.7%, respectively. Below 3000 cm^{-1} we use the measured MIR reflectance at each temperature. The uncertainty in the exact temperature dependence of the optical reflectance yields variations of the temperature dependence of the optical conductivity of the order 50%, but does not alter the general trend. We therefore take the temperature dependence as an estimate which captures the correct trend and the correct order of magnitude.

The temperature dependence of the optical transmittance at 4000 cm^{-1} is shown in Fig. 5. Although there is some scattering ($\pm 0.3\%$), one might observe that the temperature dependence at low temperatures is weak, and increases above $\sim 80-100$ K. The data present measurements in two different setups (MIR and NIR) as well as measurements where the sample and the MgO reference positions have been exchanged. Similar behavior is observed at other frequencies, and the same tendency might be observed in Fig. 6 where the differential transmittance $\mathcal{T}(T-90\ \mathrm{K})$ at several temperatures is shown. Higher transmittance at high temperatures means that the film is less absorbing in the NIR regime. These results are consistent with powder absorbance measurements where the optical absorbance increases upon cooling to T_c, then saturates or decreases with further cooling.[3,4]

The parameters used to fit the measured data at 95, 150, and 250 K are listed in Table I. Upon cooling there is a transfer of oscillator strength from the "normal Drude" to the "extended Drude" fluid, according to our phenomenological model. The dc resistivity, extrapolated from the optical data, is in fair agreement with the measured values. The zero-frequency scattering rates are found to be temperature dependent and reflect the dc data, while the frequency-dependent part g_Γ is temperature independent. The main change in the NIR regime is thus due to the temperature dependence of the plasma frequency hence of the ratio n^*/m^*, the number and effective mass of the free carriers, respectively. In the present model this variation is attributed to the transfer of oscillator strength therefore the number of free carriers in each fluid is temperature dependent: $n^*=n^*(T)$, $m^*=\mathrm{const}$.

DISCUSSION

One of the main aims of this study is to explore the temperature dependence of the NIR response below and above T_c, in order to resolve the discrepancies between reflectance and powder absorbance measurements. The results indicate some temperature dependence which is hard to observe in both reflectance and transmittance experiments, however consistent with the absorbance results. It is thus essential to understand what is measured in the absorbance experiment in order to analyze these results quantitatively. Using the measured optical constants of the Y-Ba-Cu-O films and our own absorbance data we found that effective medium approximation is sufficient to explain the absorbance spectra provided two realistic corrections are taken into account: (a) the Y-Ba-Cu-O grains have wide shape distribution, from spherical-like to platelike. Such distributions have been

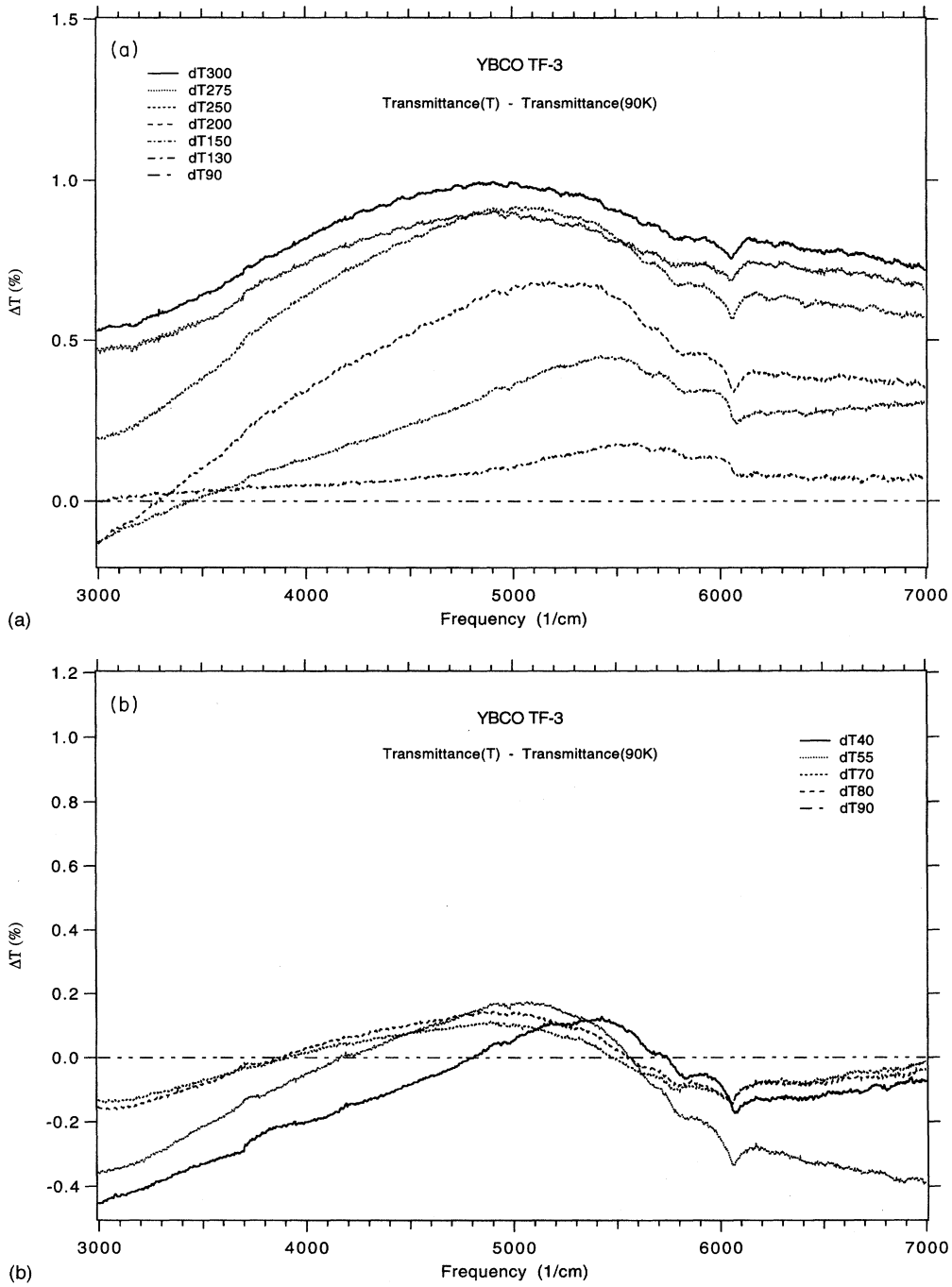

FIG. 6. Differential transmittance in the normal state (a) and the superconducting state (b). Higher transmittance at high temperatures indicate lower absorption. The dips at 6000 cm^{-1} are experimental noise due to the beam splitter.

found in TEM micrographs of Y-Ba-Cu-O powder where aspect ratios as large as 10 have been observed. (b) The KBr-Y-Ba-Cu-O pellets, used in absorbance measurements, are nonuniform hence there is a distribution of local concentration. Again this correction is consistent with observing black and white dots on the pellets, either with a naked eye or with an optical microscope (depending on the degree of mixing). The Maxwell-Garnett approximation modified to ellipsoids of different aspect ratios has the following form:[15]

$$\varepsilon_e=\varepsilon_{\mathrm{KBr}}\frac{1+(2/3)\sum_i f_i\alpha_i}{1-(1/3)\sum_i f_i\alpha_i},\qquad \alpha_i=\frac{\varepsilon_{\mathrm{YBCO}}-\varepsilon_{\mathrm{KBr}}}{L_i\varepsilon_{\mathrm{YBCO}}+(1-L_i)\varepsilon_{\mathrm{KBr}}}, \tag{6}$$

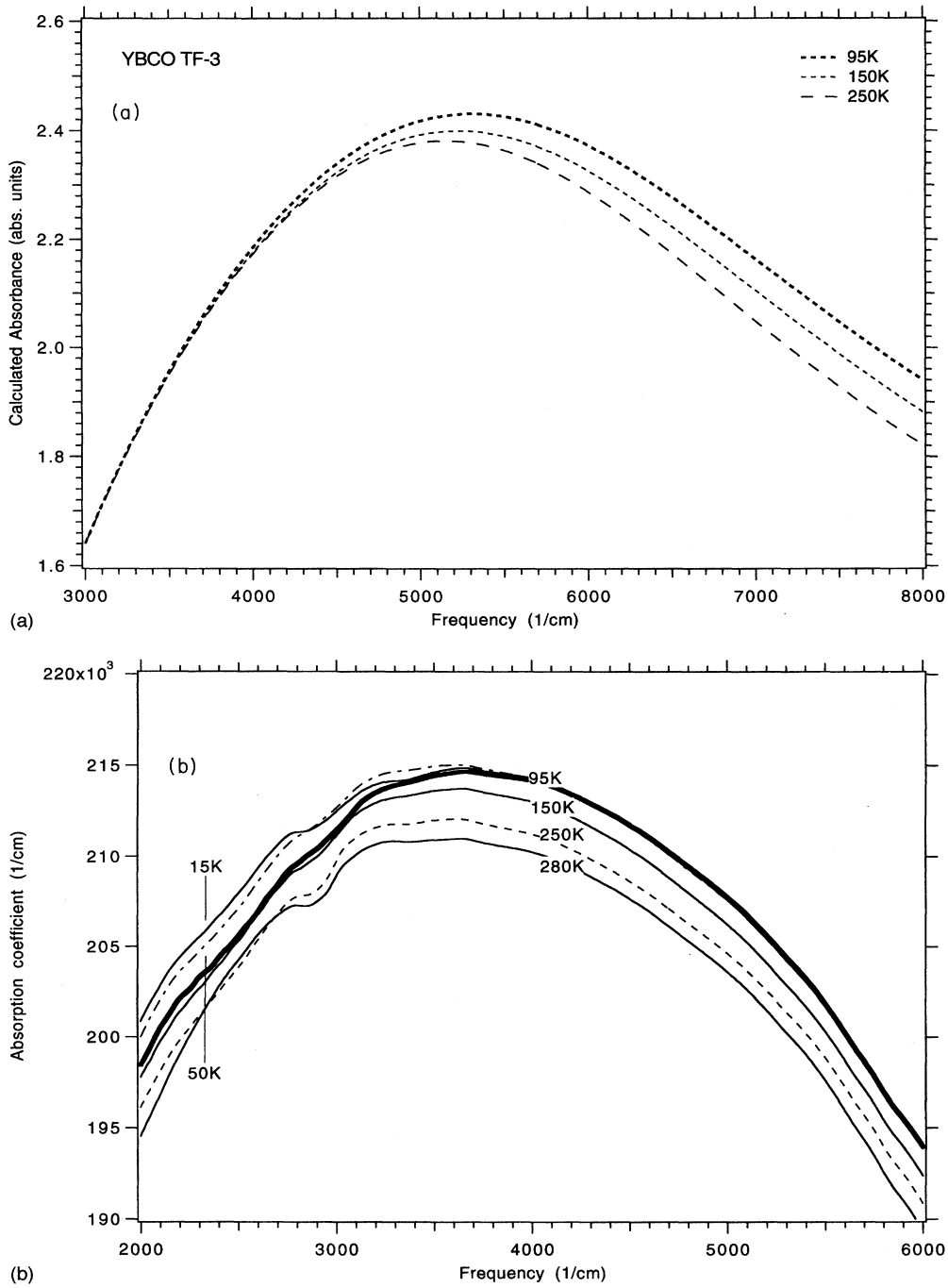

FIG. 7. (a) Calculated pellet absorbance spectra of a Y-Ba-Cu-O-KBr pellet at 95, 150, and 250 K. (b) Measured absorption coefficient of the 800 Å Y-Ba-Cu-O film at several temperatures.

where ϵ_e is the effective dielectric response of the Y-Ba-Cu-O-KBr pellet, and f_i, L_i are, respectively, the volume fraction and the depolarization factor of a subset of Y-Ba-Cu-O grains with similar geometry. For spheres $L=1/3$, $L<1/3$ for a platelike spheroid and $L>1/3$ for needlelike ones. In the present calculation a uniform distribution of depolarization factors $L=0.05-0.35$ was used. Nonuniform Y-Ba-Cu-O concentration is approximated by assuming 70% of the pellet area to be opaque (high Y-Ba-Cu-O concentration) and 30% area with local volume concentration of 0.15% Y-Ba-Cu-O. In real pellets, similar absorbance has been measured for total volume fraction of ~0.3%, where the absolute absorbance depends on the degree of mixing. Using (6) and the above parameters both frequency dependence and magnitude of the measured absorbance are recovered. It is important to note here that effective-medium approximation (EMA), by definition, does not include nonspecular scattering. Therefore at high frequencies where $\lambda \sim a$ (λ,a are the optical wave-

length and grain size, respectively) EMA would underestimate the measured absorbance. For submicron particles, typical in powder absorbance experiments, nonspecular scattering becomes significant above 10 000 cm^{-1}. In Fig. 7(a) we present the calculated pellet absorbance using the calculated dielectric response of Y-Ba-Cu-O at three temperatures (see parameter list in Table I). The results are consistent with published absorbance measurements where in the normal state the integrated absorbance increases with decreasing temperature. Below T_c both $\mathscr{R}$ and $\mathscr{T}$ are saturated within the experimental uncertainty, hence the 95 K spectrum is maintained down to zero temperature. Comparison with the measured absorption coefficient $\alpha=4\pi\omega\,\mathrm{Im}(\sqrt{\epsilon})$ at several temperatures, Fig. 7(b), shows that the pellet absorbance captures the correct temperature dependence, and that the maximum absorption in the powder data is shifted to higher energies. It is evident that powder absorbance measurements have higher sensitivity to the temperature dependence of the NIR response compared with other methods, hence the "discrepancies" between absorbance and reflectance data are just due to resolution.

The temperature dependence observed in NIR absorbance experiments has been theoretically analyzed within the general picture of a bipolaron model.[16] According to that approach, polarons and bipolarons are formed well above T_c due to strong electron-phonon interaction. The bipolarons are bosons with spin zero or one, separated by a real or pseudospin gap of the order of $4k_BT_c$. In the normal state one measures the temperature-dependent occupancy of the singlet and triplet bipolarons, which have different absorption cross sections. In the superconducting state one also measures the fraction of the condensate bosons, which are zero momentum singlets that cannot absorb light. It is interesting to compare this approach with the phenomenological model of the thin-film results. As mentioned above, the main contribution to the temperature dependence in the NIR regime is due to the transfer of oscillator strength from the "normal Drude" to the "extended Drude" fluid. Assuming that this is due to the change in number of charge carriers N_{eff}, one finds

$$\frac{\mathrm{IA}(T_1)-\mathrm{IA}(T_2)}{\mathrm{IA}(T)}\propto\frac{(\partial N/\partial T)\Delta T}{N_{\mathrm{eff}}(T)}\propto\frac{\omega_{11}\Delta T}{\omega_{10}}\approx 10\%$$

$$(300\rightarrow 100\ \mathrm{K}), \tag{7}$$

where IA is the integrated absorbance (say 4000–8000 cm^{-1}), and

$$\omega_p^{*2}=\omega_{\mathrm{ED0}}^2+\omega_{\mathrm{ED1}}|\omega|\propto N_{\mathrm{eff}};\omega_{\mathrm{ED1}}=\omega_{10}-\omega_{11}T. \tag{8}$$

The relative change in the integrated absorbance is thus a direct measure of the relative change in ω_{ED1}, with the same order of magnitude as that reported in the absorbance measurements. Since the temperature dependence in the normal state is due to the occupancy probabilities of singlet and triplet bipolarons, it is tempting to identify the extended Drude fluid as the singlet bipolaron bosons, and the normal Drude fluid as the triplet bipolarons. However, a more rigorous theoretical treatment is needed in order to compare the full dielectric response, as measured by us, with any theoretical model.

CONCLUSIONS

In this work we have presented optical data of thin Y-Ba-Cu-O films where both reflectance and transmittance have been measured. Structural analysis as well as comparison with untwinned single-crystal data suggest that the optical conductivity measured in these films is due to the Cu-O planes, and that the Cu-O chain contribution is suppressed. We find that the complex dielectric response, directly calculated from the optical data, is more complicated than any of the known models predictions. In particular, the midinfrared response cannot be presented by a wide oscillator, and both marginal- and nested-Fermi-liquid approaches are insufficient to explain the optical response of Y-Ba-Cu-O. Instead one should consider a multicomponent model or a single fluid with complicated frequency and temperature dependencies.

The temperature dependence of the MIR and NIR regimes was found to be consistent with powder absorbance measurements. In this regime the optical energy is much higher than both temperature and the superconducting energy gap, therefore the temperature dependence in the normal and in the superconducting states is anomalous and cannot be explained within a normal Fermi-liquid approach. Any theory attempting to explain these materials should consider the fact that T_c is observed at such high energies as $\omega/2\Delta>10$.

Powder absorbance measurements are found to be a reliable method in studying the optical response in the MIR and NIR regimes. Since the effective-medium approximation is sufficient to understand the absorbance data at the above spectral range, scattering and reflectance are not significant in those measurements although they are close to the limit of validity of EMA where the wavelength is of the order of the grain size.

In summary, the anomalous NIR response is a crucial test for any theory attempting to describe both normal and superconducting states of high-temperature superconductors. At present only the bipolaron model could explain the observed temperature dependence, however fully quantitative comparison cannot be made since a full description of the dielectric response is still lacking. We hope that this study will stimulate more theoretical work on the NIR response, and in particular the observation of T_c at energies so much higher compared to the superconducting energy gap.

ACKNOWLEDGMENTS

We would like to thank our colleagues in Cambridge for fruitful collaboration and stimulating discussions. In particular the help of A. S. Alexandrov, J. Chrosch, A. P. Mackenzie, P. S. De Silva, and R. Somekh is appreciated. This research was partially supported by the National Physical Laboratory (NPL).

[1] For a review, see D. B. Tanner and T. Timusk, in *Physical Properties of High Temperature Superconductors III*, edited by D. M. Ginsberg (World Scientific, Singapore, 1992), and references therein.

[2] K. Kamaras, S. L. Herr, F. Gao, B. Andraka, G. R. Stewart, D. B. Tanner, K. Remschnig, J. M. Tarascon, and S. Etemad (unpublished).

[3] H. L. Dewing and E. K. H. Salje, Supercond. Sci. Technol. **5**, 50 (1992).

[4] C. H. Ruscher, M. Gotte, B. Schmidt, C. Quitmann, and G. Guntherodt, Physica C **204**, 30 (1992).

[5] Y. Yagil and E. K. H. Salje (unpublished).

[6] F. Baudenbacher, K. Hirata, P. Berberich, H. Kinder, W. Assmann, and H. P. Lang, Physica C **185–189**, 2177 (1991).

[7] A. P. Mackenzie (private communication).

[8] J. Chrosch (private communication); C. T. Lin, J. Chrosch, Y. Yan, W. Y. Liang, and E. K. H. Salje, Physica C **242**, 105 (1995).

[9] A. K. Sarychev, D. J. Bergman, and Y. Yagil, Phys. Rev. B **51**, 5366 (1995).

[10] Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Feild, S. H. Blanton, U. Welp, G. W. Crabtree, Y. Fanf, and J. Z. Liu, Phys. Rev. Lett. **65**, 801 (1990).

[11] A. Zibold, L. Widder, H. P. Geserich, G. Brauchle, H. Claus, H. v. Lohneysen, N. Nucker, A. Erb, and G. Muller-Vogt, Physica C **212**, 365 (1993).

[12] C. M. Varma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A. E. Ruckenstein, Phys. Rev. Lett. **63**, 1996 (1989); P. B. Littlewood and C. M. Varma, J. Appl. Phys. **69**, 4979 (1991).

[13] A. Virosztek and J. Ruvalds, Phys. Rev. B **42**, 4064 (1990); J. Ruvalds and A. Virosztek, *ibid.* **43**, 5498 (1991).

[14] Z. Schlesinger, R. T. Collins, F. Holtzberg, C. Feild, G. Koren, and A. Gupta, Phys. Rev. B **41**, 11 237 (1990).

[15] C. Maxwell-Garnett, Philos. Trans. R. Soc. London **203**, 385 (1904); C. G. Granqvist and O. Hunderi, Phys. Rev. B **18**, 2897 (1978).

[16] A. S. Alexandrov, A. M. Bratkovsky, N. F. Mott, and E. K. H. Salje, Physica C **215**, 359 (1993), and references therein.