

INFRARED STUDIES OF TEXTURED CERAMIC HIGH- T_c SUPERCONDUCTORS

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The surfaces of ceramic samples of high-temperature superconductors can have a high degree of crystalline orientation, depending of the way in which they are prepared. (In particular it is essential that the sample not be polished in an attempt to “improve” the optical quality.) The surfaces of these textured ceramic samples consist of small crystallites, with about 80% orientation of the crystallographic c axis normal to the surface. The infrared and optical properties of these samples have been measured. We observe that the frequency-dependent conductivity can be decomposed into the sum of a far-infrared Drude part (which at zero frequency equals the ordinary dc conductivity) and a broad, temperature-independent mid-infrared band. The mid-infrared band has about four times the oscillator strength of the low-frequency Drude part.

In this paper we discuss the temperature-dependent infrared absorption of oriented ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. These samples show two important contributions to the frequency-dependent conductivity: a Drude part in the far infrared and a broad mid-infrared absorption. Comparing to earlier [1] studies of unoriented samples, we find the Drude contribution to be substantially stronger and the mid-infrared band at lower frequency; thus, the presence of the mid-infrared band is much less obvious than previously, particularly at room temperature. This has led to a number of authors modeling the entire infrared region with a simple Drude conductivity [2–5]. We find, however, that the temperature dependence of the mid-infrared and far-infrared conductivities are different, suggesting that different mechanisms govern the zero-frequency (dc) and the mid-infrared behavior [6].

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We measured samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared by the usual ceramic technique [7]. They were disk shaped, 1.2 cm in diameter and 0.5 to 2 mm in thickness. As discussed previously [8], the surface of an as-prepared ceramic sample can possess a high degree of orientation. Electron microscopy shows that the surface consists of a layer of small, tile-like crystals, 5 to 20 μm in size, each with its c -axis normal to the surface of the disk. Analysis of X-ray intensities shows that about 80% of the surface is covered with these oriented crystals, the remainder being largely pits or cracks. Thus, normal-incidence optical measurements orient the electric field vector largely parallel to the ab -plane of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ unit cell.

This orientation or "texturing" occurs near the surface only. Thus, polishing or other surface treatments (including exposure to moisture) have the effect of reducing the degree of orientation and thus of degrading the infrared reflectance. For example, highly textured surfaces at 100 K had a 400 cm^{-1} infrared reflectance (when corrected for the rough surfaces – see discussion below) of 85%; after polishing to produce a high gloss surface, the reflectance decreased to 65% [8].

The infrared measurements were carried out as near-normal-incidence reflectance studies using a Perkin-Elmer grating monochromator for the visible and near infrared, a Bruker/IBM infrared spectrometer for the infrared and far infrared, and a homebuilt interferometer for the far infrared. The as-prepared surfaces of the textured samples are very rough, making correction for the non-specular reflection important. This we do by coating the pellet with a metallic film (Al or Pb) and measuring the reflectance of the coated surface. By comparing this measurement to the known reflectance of the metal we obtain a first-order estimate of the fraction of the incident light scattered out of the beam. The frequency range covered was typically from 20 cm^{-1} (2.5 meV) to $20\,000\text{ cm}^{-1}$ (2.5 eV). This range is sufficient that a Kramers–Kronig analysis of the corrected reflectance can be used to determine the frequency-dependent conductivity, $\sigma_1(\omega)$, and dielectric function, $\epsilon_1(\omega)$.

Fig. 1 shows as points $\sigma_1(\omega)$ at 100 K of a textured ceramic sample. The solid line the conductivity calculated from a model dielectric function given by

$$\epsilon_n(\omega) = -\frac{\omega_{\text{pD}}^2}{\omega^2 + i\omega/\tau} + \sum_{j=1,6} \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j} + \frac{\omega_{\text{pe}}^2}{\omega_e^2 - \omega^2 - i\omega\gamma_e} + \epsilon_\infty, \quad (1)$$

where the first term is a Drude contribution characterized by plasma frequency $\omega_{\text{pD}} = 5900\text{ cm}^{-1}$ (0.74 eV) and relaxation rate $1/\tau = 300\text{ cm}^{-1}$ (0.037 eV); the second is from six optical phonons, [9, 10] with frequencies ω_j , damping constants γ_j , and oscillator strengths S_j ; the third the contribution of the mid-infrared absorption band, represented by an overdamped oscillator with

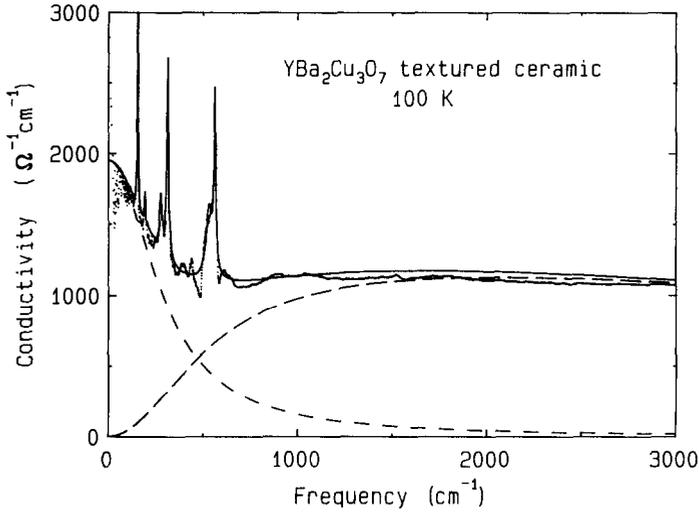


Fig. 1. Frequency-dependent conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 100 K. A fit of the data to eq. (1) is also shown.

center frequency $\omega_c = 2100 \text{ cm}^{-1}$ (0.26 eV), strength $\omega_{pe} = 21,000 \text{ cm}^{-1}$ (2.6 eV), and width $\gamma_c = 8400 \text{ cm}^{-1}$ (1 eV); the last the high-frequency value of ϵ_1 , here taken to be $\epsilon_\infty = 3.8$. (Note that the parameters given above were obtained by fitting to the measured reflectance.) Fig. 2 also shows as dashed lines the contributions to $\sigma_1\omega$ of the far-infrared Drude term and the mid-infrared absorption.

The Drude part is responsible for the far infrared conductivity, but by 400 cm^{-1} or so the mid-infrared band dominates. With increasing temperature, the Drude contribution decreases in amplitude and broadens (in agreement with σ_{dc}). The dc conductivity determined by far infrared means ($2000 \text{ } \Omega^{-1} \text{ cm}^{-1}$) is about 2/3 of the measured dc conductivity of this sample; however, the temperature dependence shows the expected behavior, being $\sigma_{dc} \sim 1/T$ from 100 to 300 K [11, 12]. Fig. 2 shows $\sigma_1(\omega)$ at several temperatures. Evident is the contrast between the rather strong temperature dependence of the far-infrared Drude conductivity and the very weak temperature dependence of the mid-infrared conductivity.

Fig. 3 shows $\epsilon_1(\omega)$ at 100 and 300 K. Note that $\epsilon_1(\omega)$ is negative at low frequencies (as appropriate for a conductor) but then rises and is nearly zero above about 800 cm^{-1} . (At 300 K, $\epsilon_1 > 0$ while at 100 K, $\epsilon_1 < 0$.) The frequency where $\epsilon_1(\omega)$ becomes small is much lower than the 5900 cm^{-1} Drude plasma frequency, due to screening by the mid-infrared absorption processes.

We have taken the point of view in this paper that the Drude and mid-infrared contributions to $\sigma_1(\omega)$ are two distinct terms, perhaps involving

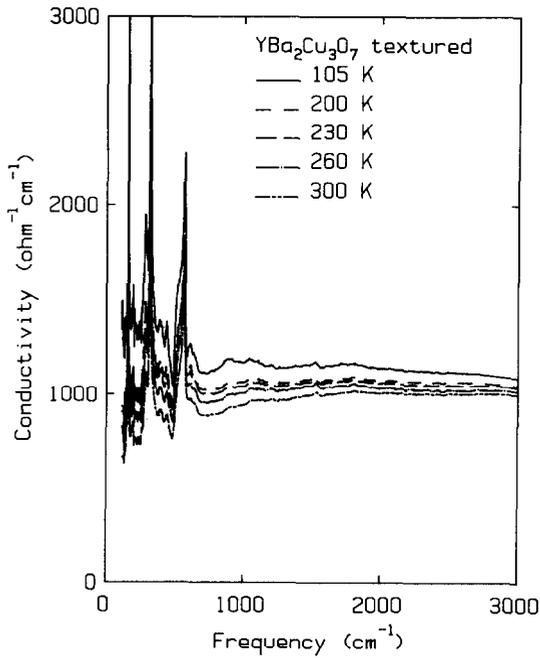


Fig. 2. Frequency-dependent conductivity at several temperatures.

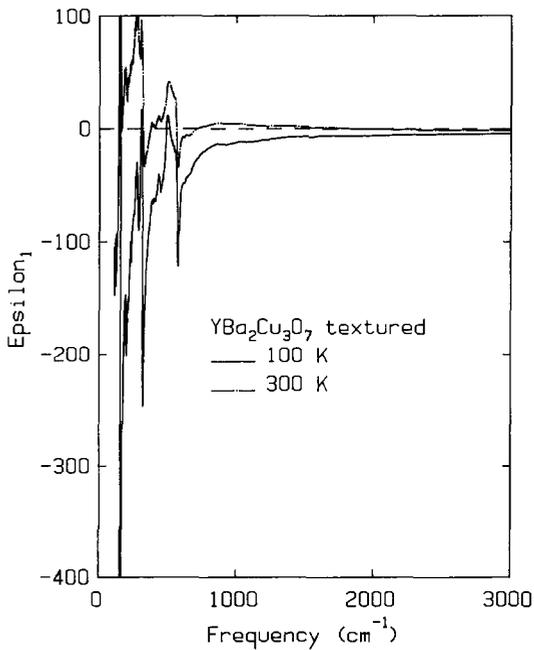


Fig. 3. Real part of the complex dielectric function at 100 and 300 K.

different charge carriers. Now, we discuss whether we could also fit our data by including in the Drude term of eq. (1) a frequency-dependent relaxation rate $\gamma_D(\omega) = 1/\tau$ and effective mass $m^*(\omega) = 4\pi ne^2/\omega_{pD}^2$ and by omitting entirely the term due to the mid-infrared absorption band. Such an analysis has been suggested recently [13, 3]. (Both $\gamma_D(\omega)$ and $m^*(\omega)$ must be included in order that the resulting dielectric function satisfy the Kramers–Kronig relations.) After a little algebra, eq. (1) can be inverted to yield

$$\gamma_D(\omega) = \frac{4\pi\sigma_1(\omega)}{\varepsilon_x + \varepsilon_{\text{phonon}}(\omega) - \varepsilon_1(\omega)} \quad (2)$$

and

$$\frac{4\pi ne^2}{m^*(\omega)} = [\varepsilon_x + \varepsilon_{\text{phonon}}(\omega) - \varepsilon_1(\omega)][\omega^2 + \gamma_D^2]. \quad (3)$$

Here, n is the concentration of free carriers and $\varepsilon_{\text{phonon}}(\omega)$ is the contribution to the dielectric function of the j vibrational modes. This is significant only at frequencies near the phonon frequencies, although it does add a positive contribution to the static dielectric constant.

For eqs. (2) and (3) to be applicable the term $\varepsilon_x + \varepsilon_{\text{phonon}}(\omega) - \varepsilon_1(\omega)$ must be positive, else a negative relaxation rate be found. In our data, this is true at 100 K but false at 300 K, on account of the reduced oscillator strength of the Drude contribution at room temperature. Thus we are *unable* to account for our data at all temperatures in terms of a frequency-dependent $\gamma_D(\omega)$ and $m^*(\omega)$.

In summary, our studies of the temperature dependence of the infrared properties of textured ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ point to two distinct contributions to the electronic properties: a Drude contribution from free carriers in the far infrared and a broad mid-infrared absorption.

Acknowledgments

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References

- [1] K. Kamarás, C.D. Porter, M.G. Doss, S.L. Herr, D.B. Tanner, D.A. Bonn, J.E. Greedan, A.H. O'Reilly, C.V. Stager and T. Timusk, Phys. Rev. Lett. 59 (1987) 919.

- [2] I. Bozovic, D. Kirilov, A. Kapitulnik, K. Char, M.R. Hahn, M.R. Beasley, T.H. Geballe, Y.H. Kim and A.J. Heeger, *Phys. Rev. Lett.* 59 (1987) 2219.
- [3] Z. Schlesinger, R.T. Collins, D.L. Kaiser and F. Holtzberg, *Phys. Rev. Lett.* 59 (1987) 1958.
- [4] J. Orenstein, G.A. Thomas, D.H. Rapkine, C.B. Bethea, B.F. Levine, B. Batlogg, R.J. Cava, D.W. Johnson, Jr. and E.A. Reitman, *Phys. Rev. B* 36 (1987) 8892.
- [5] J. Orenstein and D.H. Rapkine, *Phys. Rev. Lett.* 60 (1988) 968.
- [6] K. Kamarás, C.D. Porter, M.G. Doss, S.L. Herr, D.B. Tanner, D.A. Bonn, J.E. Greedan, A.H. O'Reilly, C.V. Stager and T. Timusk, *Phys. Rev. Lett.* 60 (1988) 969.
- [7] D.A. Bonn, J.E. Greedan, C.V. Stager, T. Timusk, M.G. Doss, S.L. Herr, K. Kamarás and D.B. Tanner, *Phys. Rev. Lett.* 58 (1987) 2249.
- [8] D.A. Bonn, A.H. O'Reilly, J.E. Greedan, C.V. Stager, T. Timusk, K. Kamarás and D.B. Tanner, *Phys. Rev. B* 37 (1988) 1547.
- [9] M.K. Crawford, W.E. Farneth, R.K. Brodia and E.M. McCarron III, *Phys. Rev. B* 37 (1988) 3371.
- [10] S. Sugai, *Phys. Rev. B* 36 (1987) 7133.
- [11] M. Gurvitch and A.T. Fiory, *Phys. Rev. Lett.* 59 (1987) 1337.
- [12] T. Timusk, D.A. Bonn, J.E. Greedan, C.V. Stager, J.D. Garrett, A.H. O'Reilly, M. Reedyk, K. Kamarás, C.D. Porter, S.L. Herr and D.B. Tanner, *Proc. of Int. Conf. on High Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken 1988*, *Physica C* 153–155 (1988) 1744.
- [13] J. Orenstein, G.A. Thomas, D.H. Rapkine, A.J. Millis, L.F. Schneemeyer and J.V. Waszczak, *Proc. of Int. Conf. on High Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken 1988*, *Physica C* 153–155 (1988) 1740.