

Vibrational structure in the infrared reflectance spectra of the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ¹

K. Kamarás *

Central Research Institute for Physics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest (Hungary)

S.L. Herr

Physics Department, Virginia Commonwealth University, Richmond, VA 23220 (U.S.A.)

C.D. Porter and D.B. Tanner

Department of Physics, University of Florida, Gainesville, FL 32611 (U.S.A.)

S. Etemad and J.-M. Tarascon

Bell Communications Research, Red Bank, NJ 07701 (U.S.A.)

(Received 20th April 1990)

Abstract

Pressed ceramic pellets of the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($T_c = 85$ K) were investigated by reflectance spectroscopy in the infrared and visible regions at several temperatures both below and above the superconducting transition. In the process of identifying and analyzing vibrational lines in these samples, two problems arise: diffuse scattering connected with the grainy surface and a non-conventional baseline caused by intense absorption of the electronic background present in the infrared region. After eliminating the effects due to these processes, the temperature dependence of the vibrational lines can be extracted. It is concluded that none of the lines behaves in an anomalous way, i.e., no vibration strongly coupled to the electronic system was found.

Keywords: Infrared spectrometry; Superconductors; Vibrational structure

Vibrational spectroscopy has been intensively used to study high-temperature superconductors since their discovery [1]. Most of the work has been done on $\text{YBa}_2\text{Cu}_3\text{O}_7$ analogues. In this work, the temperature dependence of the vibrational lines derived from infrared and visible spectra of the high- T_c superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ was studied.

¹ Presented at the *Austrian–Hungarian Conference on Recent Developments in Infrared and Raman Spectroscopy, Veszprém, Hungary, April 18–20, 1990*. The majority of the papers presented at this symposium have been published in *Vibrational Spectroscopy*, Vol. 1, No. 2 (1990).

EXPERIMENTAL

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ was prepared from Bi_2O_3 , SrCO_3 , CaCO_3 and CuO as described [2]. The investigated pellet showed a superconducting transition temperature $T_c = 85$ K, as determined by measurement of the a.c. susceptibility, and about a 30% Meissner effect.

Reflection spectra in the infrared region ($160\text{--}5000\text{ cm}^{-1}$) were measured with a Bruker FTS 113v spectrometer equipped with a specular reflectance insert, and a laboratory-made spectro-meter based on a Perkin-Elmer grating monochromator was used from the near-infrared to the ultraviolet

region ($2000\text{--}20\,000\text{ cm}^{-1}$). Low-temperature measurements were performed in an Air Products continuous-flow helium cryostat.

Owing to diffuse scattering from the grainy surface of the pellet, spectra taken against a standard reference mirror are strongly distorted, especially at higher frequencies. Earlier experience indicated that polishing leads to irreversible deterioration of the surface layer, so, in order to eliminate this effect, the following procedure was used: after the measurement, a layer of aluminium was deposited on the sample, thin enough to keep the original surface structure but thick enough not to be transparent. The thickness to satisfy both requirements proved to be $1000\text{--}2000\text{ Å}$ from initial experiments. In the present case, a 2000-Å thick coating was applied by ion milling in a Veeco Microetch. The spectrum of the coated sample was measured in exactly the same geometry as for the uncoated sample, and the ratio R (uncoated)/ R (coated) was used for quantitative studies (e.g., Kramers–Kronig analysis), corrected for the known reflectivity of aluminum. In Fig. 1 the process is illustrated and the results are compared with the reflectivity of a single crystal of the same material [3]. The agreement with the single-crystal data is more than satisfactory; the differences can be attributed to the fact that the

material is strongly anisotropic and the crystal plates normal to the incident light are oriented in the ab plane.

Optical conductivity was calculated from the reflectivity by Kramers–Kronig analysis [4]. Standard extrapolations were used at frequencies higher than $20\,000\text{ cm}^{-1}$; the details had virtually no effect on the conductivity below 1000 cm^{-1} . At low frequencies a metallic extrapolation $R = 1 - A\sqrt{\omega}$ was applied in the normal state, whereas below T_c the reflectivity was made to approach unity by using the equation $R = 1 - B\omega^4$ (A and B are fitting constants). As these extrapolations introduce an ambiguity into the analysis, the method of fitting the measured reflectivity to that derived from an assumed model dielectric function was also used. The model used was a sum of a Drude term and several Lorentz oscillators; the starting values for the fit were estimated from the Kramers–Kronig optical conductivity curves [5].

RESULTS AND DISCUSSION

In the widely studied $\text{RBa}_2\text{Cu}_3\text{O}_7$ materials, two types of anomalous temperature dependence of vibrational lines have been found. One is a small red shift (“softening”) of one line below T_c with decreasing temperature, for which a theoretical model has been developed by Zeyher and Zwicknagl [6], assuming strong electron–phonon coupling. The other is a sudden increase in the line width on going from the superconducting to the normal state [7]. This has been attributed to interaction of the vibrations with the metallic electrons, causing an anomalous broadening in the normal state but disappearing when the electrons condense into the superconducting δ -function at zero frequency [8]. In this study, none of the vibrational modes showing these anomalies could be detected.

Fig. 2 shows reflection spectra measured at six temperatures between 20 and 300 K. Within experimental error, because of the very large line widths, no change is apparent. In order to extract the vibrational parameters more precisely, an oscillator fit was performed over the whole spectral range. The model [5] took into account the

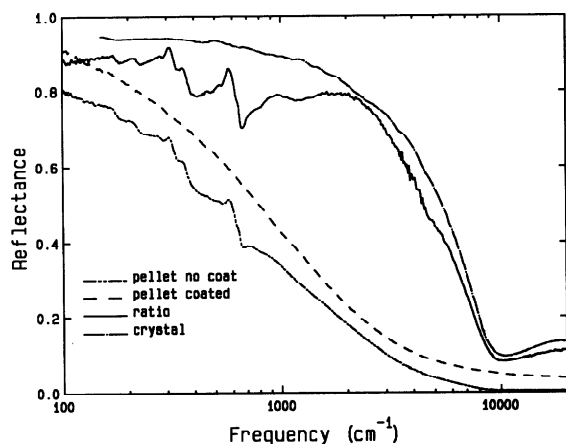


Fig. 1. Reflectivity vs. frequency for a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ pellet at room temperature before and after coating with aluminum, and the ratio of the two spectra compared with that of a single crystal of the same composition. Note the logarithmic frequency scale.

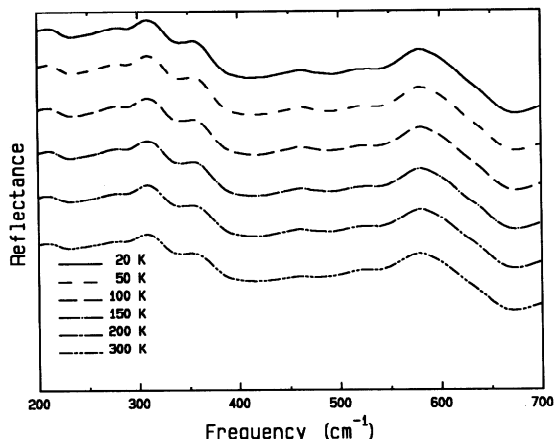


Fig. 2. Reflectivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (corrected for scattering losses) at six temperatures. The curves have been shifted along the vertical axis for clarity.

effect of the metallic electrons (a Drude term), excitations of bound electrons in the infrared region (broad Lorentzians) and vibrational transitions (narrow Lorentzians). The 300 K optical conductivity is depicted in Fig. 3, together with the first two types of lines. Without this electronic background, vibrational frequencies derived from such a fit should correspond exactly to peaks in the optical conductivity, but the slope of the background causes the peaks to shift. Fig. 4 shows the optical conductivity (directly derived from the reflectivity curves) at three temperatures; in Fig. 5

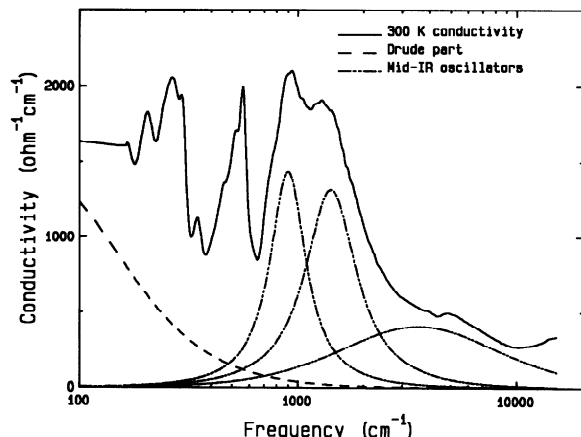


Fig. 3. Optical conductivity vs. frequency of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ at 300 K. Electronic contributions were obtained by an oscillator fit described in the text. Note the logarithmic frequency scale.

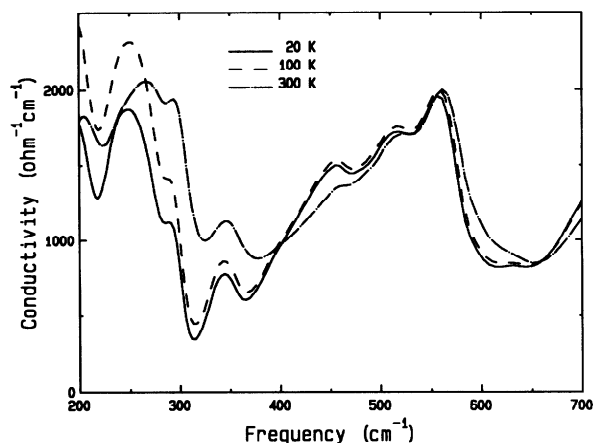


Fig. 4. Optical conductivity vs. frequency of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ at three temperatures.

the very strongly temperature-dependent Drude term has been subtracted in order to make the vibrational contributions comparable. The broad mid-infrared excitations have very little temperature dependence, hence they do not affect the variation of the vibrational lines with temperature; however, the apparent peak positions differ from those obtained by the fit because of the sloping baseline.

Peak positions derived from the fit at 300 K are 260, 294, 349, 447, 515 and 563 cm^{-1} , showing some discrepancy with the data published by Piro et al. [9] in the 500–600 cm^{-1} region. The dif-

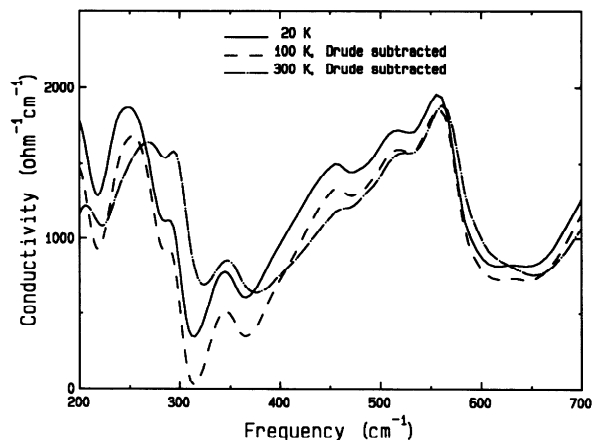


Fig. 5. Optical conductivity vs. frequency for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, with the Drude contributions of the free electrons subtracted.

ference may be caused by their not taking into account scattering effects. Some of the weaker lines may originate from other phases present in the sample, but these do not affect the validity of the present results concerning the temperature dependence.

Popovic et al. [10], in a study of the analogous compound $\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_6$, observed a line at 490 cm^{-1} , showing an appreciable blue shift between 10 and 300 K. They attributed this change to the opening of a superconducting energy gap near this frequency. In the present case there is also a strong shift, especially for the low-frequency modes, but the change takes place in the normal state (between 100 and 300 K) and not on going through the superconducting transition. Hence it seems that no particular phonon can be singled out showing correlations with superconductivity in this material. The results of the Drude-Lorentz fits to the reflectivity support this conclusion: frequencies and line widths for all modes are essentially constant below T_c , and above T_c both the frequencies and the line widths increase with increasing temperature. The frequency shift in the normal state is unusual in itself and indicates that the coupling of vibrations to low-energy electronic excitations has to be taken into account in a more complex way.

The authors thank Drs. B. Andraka and G.R. Stewart for the magnetic susceptibility measure-

ments. The work at the University of Florida was supported by DARPA through contract MDA972-88-J-1006.

REFERENCES

- 1 C. Thomsen and M. Cardona, in D.M. Ginsberg (Ed.), *Physical Properties of High temperature Superconductors*, World Scientific, Singapore, 1989, p. 409.
- 2 J.M. Tarascon, W.R. McKinnon, P. Barboux, D.M. Hwang, B.G. Bagley, L.H. Greene, G.W. Hull, Y. LePage, N. Stofel and M. Giroud, *Phys. Rev. B*, 38 (1988) 8885.
- 3 K. Kamarás, S.L. Herr, J.S. Kim, G.R. Stewart, D.B. Tanner and T. Timusk, *International Winter School on Electronic Properties of High Temperature Superconductors*, Kirchberg, Austria; to be published in *Springer Series in Solid-State Sciences*.
- 4 F. Wooten, *Optical Properties of Solids*, Academic, New York, 1972.
- 5 T. Timusk and D.B. Tanner, in D.M. Ginsberg (Ed.), *Physical Properties of High Temperature Superconductors*, World Scientific, Singapore, 1989, p. 339.
- 6 R. Zeyher and G. Zwicknagl, *Z. Phys. B*, 78 (1990) 175.
- 7 F. Gao, D.B. Tanner, D.A. Bonn, J.E. Greedan, C.V. Stager and T. Timusk, *Bull. Am. Phys. Soc.*, 34 (1989) 1036.
- 8 M. Tinkham, *Introduction to Superconductivity*, McGraw-Hill, New York, 1975.
- 9 O.E. Piro, J.A. Glüda, N.E. Massa, P.J. Aymonino, E.E. Castellano, H.C. Basso, J.N.H. Gallo and A.A. Martin, *Phys. Rev. B*, 39 (1989) 7255.
- 10 Z.V. Popovic, C. Thomsen, M. Cardona, R. Liu, G. Stanislav, R. Kremer and W. König, *Solid State Commun.*, 66 (1988) 965.