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Superconducting energy gap in MBa$_2$Cu$_3$O$_{7-\delta}$-type materials

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We present a far-infrared study of ceramic superconductors of the MBa$_2$Cu$_3$O$_7$ family with M = Dy, Sm$_{0.5}$Ho$_{0.5}$, and Sm$_{0.5}$Y$_{0.5}$. Emphasis is placed on the determination of the position of the superconducting energy gap E_g and its temperature dependence. We find that for all compositions studied $E_g/k_BT_c \approx 3.2 \pm 0.3$. We also find indications of the temperature dependence of the gap and discuss the influence of the phonon features on the quantitative determination of the gap position.

The determination of the energy gap and its temperature dependence are central issues in the fast developing field of high-T_c superconductivity. Several recent contributions report results of far-infrared (FIR) and electron tunneling spectroscopy in La$_{1-x}$Sr$_x$Cu$_2$O$_4$ (Refs. 1 and 2) and YBa$_2$Cu$_3$O$_{7-\delta}$.[3-9] The presence of a gap is concluded from the characteristic decrease of the FIR reflectance above a specific energy and from the V-I curves of tunneling junctions below T_c. However, the exact determination of the gap position is difficult. Tunneling spectroscopy data only recently started to give converging results.[4,10,11] Difficulties in obtaining clean surfaces in ceramic materials are probably the reason for the wide discrepancy of experimental results from different groups. Another problem plagues FIR measurements. Besides the generally poor quality of polycrystalline samples, the spectral range where the gap is found overlaps the frequencies of iractive phonons, a fact which makes unambiguous interpretation of features in the reflectance spectra difficult. In addition, rough surfaces lead to Rayleigh scattering which increases with frequency and lowers the measured reflectivity at higher frequencies with a corresponding decrease in the sensitivity of the measurements.

The present Rapid Communication reports results of FIR reflectance measurements of selected samples of the MBa$_2$Cu$_3$O$_{7-\delta}$ family with M = Dy, Sm$_{0.5}$Y$_{0.5}$, and Sm$_{0.5}$Ho$_{0.5}$. The experimental techniques have been described elsewhere. The samples were prepared by standard methods.[12] All show a sharp resistive transition at about 90 ± 2 K (92 K onset, 87 K zero resistance) and have a relatively high reflectance at low frequency (~ 30 cm^{-1}, $R \geqq 94\%$), which indicates a rather good quality of their surface (except for roughness). All samples were measured "as pressed" without any additional treatment of the surface.

Earlier studies have shown that replacement of yttrium by a lanthanide leads to the downshift of the phonon frequency observed at ~ 193 cm^{-1} for YBa$_2$Cu$_3$O$_{7-\delta}$ (Refs. 3 and 8) to about 163 cm^{-1},[13] thus providing a "cleaner" access to the interesting frequency range around 200 cm^{-1} where the gap seems to appear. It is also expected that in mixed crystals of Sm$_{0.5}$Y$_{0.5}$Ba$_2$Cu$_3$O$_{7-\delta}$ the phonon associated with the vibration of the M ion[13] should "smear out" thus making the gap region more accessible to precise measurements, in particular of its temperature dependence.

In Fig. 1 we show the reflectance spectra of DyBa$_2$Cu$_3$O$_{7-\delta}$ at 300 and 10 K. The increase of reflectance below 200 cm^{-1} at low temperature is evident. In fact, the main increase takes place between 90 and 40 K. Above and below this temperature range, the low-frequency spectra remain practically unchanged. Thin arrows in Fig. 1 indicate phonon features. Their assignments have been presented elsewhere.[13,14] It is shown below that at 10 K the low-frequency phonons, below 200 cm^{-1}, correspond to dips in reflectance, while those above 250 cm^{-1} correspond to peaks. This is not the case at 300 K where *all* phonons peak "up." As shown below, such behavior at low temperature is a direct consequence of the presence of a superconducting gap. Similar changes with

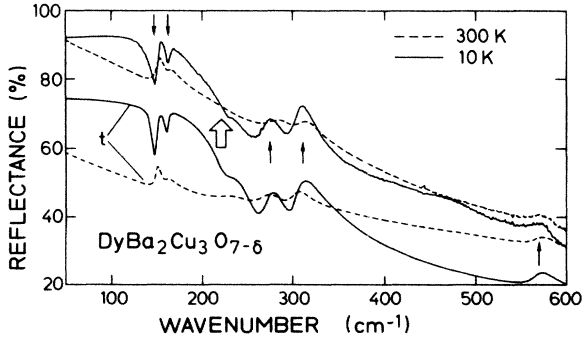

FIG. 1. Reflectance spectra of DyBa$_2$Cu$_3$O$_{7-\delta}$ between 50 and 600 cm^{-1}. Thin arrows indicate phonon features, thick arrow indicates the gap energy region at low temperature. Theoretical fit marked t is shifted down, for clarity purposes, by 20% with respect to the experimental data.

T in the phonon spectra have also been observed in FIR studies of MBa$_2$Cu$_3$O$_{7-\delta}$ with M=Y, Nd, Sm, Eu, Gd, Tb, Ho, and Er.[8,13,15] The spectra for the Sm$_{0.5}$Y$_{0.5}$ and Ho$_{0.5}$Y$_{0.5}$ compounds look very similar to the one presented in Fig. 1, only the phonon line at $\sim$163 cm^{-1} is much weaker for the Sm-Y sample, due to the mentioned smearing out in mixed crystals.

Standard ways of determining the position of the energy gap in superconductors include the analysis of the temperature dependence of the surface impedance (or reflectance) in the proper frequency range[16] and also the fit of the experimental results to model calculations based on the Mattis-Bardeen[17] theory of electromagnetic wave absorption in superconductors. Both approaches have been used here.

In Fig. 2 the low-T reflectance of the Sm$_{0.5}$Y$_{0.5}$ sample divided by that at 100 K is plotted for several temperatures between 90 and 10 K in the 150–240 cm^{-1} frequency range. Features at 175 cm^{-1} are due to changes in phonon peaks with temperature. Note the characteristic decrease of reflectance below the "normal" state value above about 200 cm^{-1}. Note also that the frequency (energy) at which the reflectance crosses the value at 100 K, which corresponds to the ratio of 1 in Fig. 2, is temperature dependent and *decreases* with *increasing* temperature. The energy $E_c(T)$ divided by $E_c(0)$ is displayed versus reduced temperature in Fig. 3. Data for the Sm$_{0.5}$Ho$_{0.5}$ sample are within experimental errors the same as for Y$_{0.5}$Sm$_{0.5}$. The solid line in Fig. 3 corresponds to the theoretical prediction of the $E_g(T)$ dependence in the BCS theory.[18] Although in an ideal Bardeen-Cooper-Schrieffer (BCS) superconductor the gap energy would show up as a maximum of the ratio of superconducting and normal-state reflectances,[17] in the present case the phonon lines make an unambiguous determination of such a maximum difficult. Therefore E_c may be treated as an approximate upper bound of the E_g value. In the same sense $E_c(T)$ gives only a rough indication of the temperature dependence of the gap. Still, our results for the Sm$_{0.5}$Y$_{0.5}$ and Sm$_{0.5}$Ho$_{0.5}$ sample suggest a much steeper temperature dependence of the gap close to T_c than the standard BCS theory. These results are in agreement with recent NMR work for Y^{89} in YBa$_2$Cu$_3$O$_{7-\delta}$ (Ref. 19) which shows that the nuclear-spin relaxation rate drops much faster near T_c than prediced by the BCS theory, thus suggesting that the number of unpaired electrons available for the spin-spin relaxation process drops very fast immediately below T_c.

Collins *et al.*[9] have recently studied the temperature dependence of the FIR reflectance of YBa$_2$Cu$_3$O$_{7-\delta}$ oriented films and bulk polycrystalline samples. They reported no evidence for a reduction of the gap very close to T_c. We notice that in YBa$_2$Cu$_3$O$_{7-\delta}$ phonons related to the vibration of the Y atoms lie very close to the low-T gap energy thus making the analysis of spectra more difficult than in the case of lanthanide compounds.

In order to obtain quantitative information about the position of the gap we fit our reflectance spectra using a model dielectric function for the superconductor. We assume the extreme dirty limit[20] of Mattis and Bardeen's equation of the dielectric function for the superconductor and standard Lorentzians for the phonons.[8] At 0 K such a model allows us to fit our reflectance spectra provided we assume that some part of the sample remains nonsuperconducting (but metallic) to the lowest temperatures. Such an assumption is supported by Meissner effect measurements which indicate that $\sim$20% of the sample remains paramagnetic. A Drude contribution is assumed for this nonsuperconducting component. Following the approach used already by Thomas *et al.*,[5] we introduce a simple form of the composite medium theory. With E_g=215 cm^{-1}, and the f_s fraction of the superconducting phase equal to $\sim$0.8 we obtain the fit shown in Fig. 1. Other parameters of the fit are shown in Table I. Note that the fit reflects well the main features of the spectrum and clearly shows the inversion of phonon features at en-

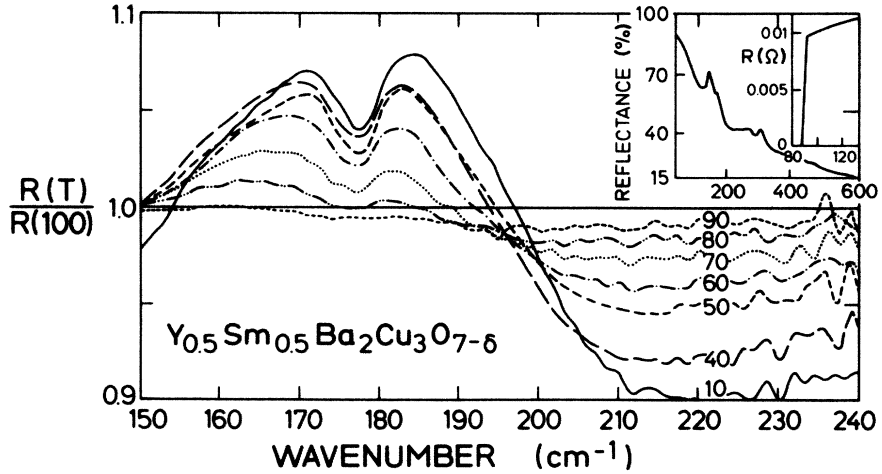

FIG. 2. Low-temperature reflectance spectra of Y$_{0.5}$Sm$_{0.5}$- Ba$_2$Cu$_3$O$_{7-\delta}$ between 150 and 240 cm^{-1}, normalized to the 100 K spectrum. The drop of the low-temperature reflectance, at approximately 200 cm^{-1} at 10 K, is interpreted as a manifestation of the gap. Features at $\sim$175 cm^{-1} are due to changes with temperature in phonon peak position. Insets show low-temperature reflectance between 50 and 600 cm^{-1} and the temperature dependence of the dc resistance.

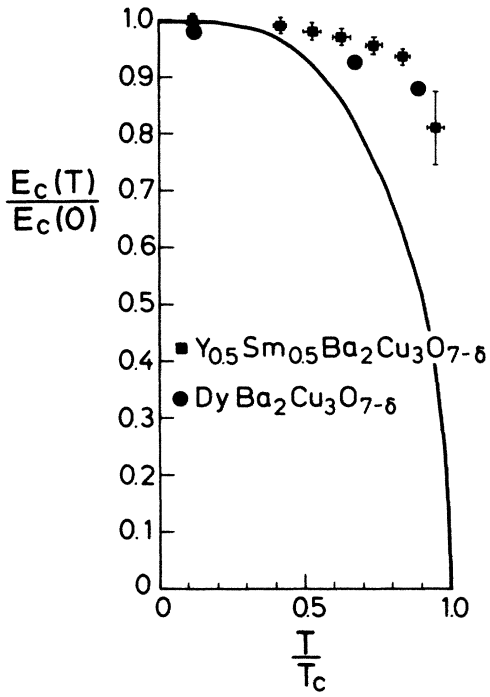

FIG. 3. Energy, $E_c(T)$, at which the low-temperature reflectance drops to its 100 K value plotted vs temperature for $Y_{0.5}Sm_{0.5}Ba_2Cu_3O_{7-\delta}$ and $DyBa_2Cu_3O_{7-\delta}$. The energy is shown in $E_c(0)$ units, the temperature in T_c units. For comparison, the picture also shows the normalized $E_g(T)$ as predicted by the BCS theory (solid line).

ergies below the gap. The fit also yields phonon linewidths and confirms the conclusion that the halfwidth of the phonons at 150 cm^{-1} and $\sim$163 cm^{-1} are a factor of 4–5 smaller than those near 270, 300, and 570 cm^{-1}. Additionally, the linewidth of the phonon at 163 cm^{-1} decreases between 300 and 10 K by a factor of 2, while the width of the phonon at 150 cm^{-1} remains almost unchanged. There are several contributions responsible for these linewidths. Normally, the phonon lifetimes are determined by an anharmonic decay due to multiphonon processes which should be strongly temperature dependent. In a normal metal, an additional weakly temperature-dependent decay process might occur by means of electron-hole excitations across the Fermi level if the transition-matrix elements allow this.[21] In a superconductor, however, there are restrictions to the latter processes: they are only effective for phonon energies higher than the gap. This may account for the sharpening of the 163 cm^{-1} phonon in the superconducting state with respect to that at 300 K (Table I).

TABLE I. Parameters used for the fits of Fig. 1 to the measured reflectance spectra at $T=10$ K. The parameters change little with temperature except for the width of the phonon No. 2. Fit parameter ($DyBa_2Cu_3O_{7-\delta}$): $E_g=215$ cm^{-1} (plasma frequency $=8000$ cm^{-1}), $T_c=90$ K (relaxation rate $=7000$ cm^{-1}), $f_s=0.8$ (dielectric constant $=4$).

Phonon	Frequency (cm^{-1})	Halfwidth (cm^{-1})	Oscillator strength
1	150	5.0	1.8
2	163	4.5 (10 K)/9.0 (300 K)	0.6
3	230	35.0	1.0
4	270	25.0	1.2
5	303	20.0	0.9
6	567	25.0	0.1

A phonon at 163 cm^{-1} has been attributed to the vibration of Dy atoms and at 150 cm^{-1} to vibrations of the Ba atoms. The distance r_{Ba} between Ba atoms and $Cu_2O(II)O(III)$ planes, where free carriers seem to be localized,[22] is significantly larger than the distance between these planes and Dy atoms r_{Dy}. Describing in the simplest approach the electron-phonon interaction by a Coulomb potential $U_M=Z_M/r_M$, where $M=$Ba, Dy, and Z_M is $2e$ for Ba and $3e$ for Dy, we obtain the ratio of $(U_{Dy}/U_{Ba})^2=4.2$ for decay rates of the Dy and Ba vibrations. Moreover, each Ba atom has only one neighboring $Cu_2O(II)O(III)$ plane while Dy has two. Also the vibrational amplitudes of each Ba atom have a factor of $(\frac{1}{2})^{1/2}$, because of eigenvector normalization. This gives additional factors to the interaction potentials, yielding finally a decay rate order of magnitude smaller for the Ba vibrations than for those of Dy. Hence, we would not expect to see any effect of the superconducting transition on the Ba-related vibrations, in agreement with our experiments. This gives additional support to the hypothesis that superconductivity occurs in the $Cu_2O(II)O(III)$ planes.[22]

Finally, the large anisotropy of the electronic properties[9,22] might cause different decay of the phonons with eigenvectors either parallel or perpendicular to the copper-oxide planes.

We have also attempted to fit the temperature dependence of the reflectance spectra. For that we assumed a temperature dependence of the superconducting fraction as $f_s(T)=f_s(1-t^4)$, where t is the reduced temperature T/T_c. Such a fit still requires temperature-dependent electronic relaxation rates and plasma frequencies (also below T_c). While such dependence cannot be discarded,[23] its origin is, at present, not clear. Comparing the fit for 300 K with an experiment, we find also a discrepancy in the overall slope of the spectrum. In a recent study of far-infrared properties of sintered $La_{1.85}Sr_{0.15}CuO_{4-y}$, Sulewski, Noh, McWhirter, and Sievers[24] have proposed that such a deviation from the Drude conductivity can be attributed to the predominantly two-dimensional character of the carriers leading to a frequency-dependent relaxation rate.[24] A two-dimensional ansatz indeed improves our fit.[15] This may be also a further indication of the anisotropy of electronic properties in $MBa_2Cu_3O_{7-\delta}$, in agreement with recent findings.[9,25]

In conclusion, we have studied the far-infrared reflectance spectra of $MBa_2Cu_3O_{7-\delta}$ superconductors with $M=$Dy, Ho-Y, Ho-Sm. In all materials investigated we find an energy gap at about 200–230 cm^{-1} which is consistent with the values reported for $YBa_2Cu_3O_{7-\delta}$.[3–8] The shape of the low-T spectrum can be fitted with a standard model based on the BCS theory.[17] We also find indications of the temperature dependence of the gap.

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