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Sharp optical lines in rare-earth barium copper oxides

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We report the results of a sensitive technique of optical spectroscopy applied to bulk and thin-film samples of the high-T_c superconductor $R\mathrm{Ba_2Cu_3O_{7-x}}$ with R = Er, Ho, and Yb. Sharp crystal electric field lines were observed in these samples at 77 and 4.2 K due to impurities of less than 1% of the so-called "green phase," $R_2\mathrm{BaCuO_5}$. Expected strong magnetic dipole transitions in the superconductor were not observed, probably because of strain broadening of the energy levels involved. The method can reveal absorption lines corresponding to oscillator strengths of 10^{-10}, for expected linewidths, in opaque or thin-film samples.

I. INTRODUCTION

Since the discovery of high-T_c superconductivity in the oxygen-deficient perovskite $\mathrm{YBa_2Cu_3O_{7-x}}$, a number of researchers have demonstrated superconductivity in the class of compounds $R\mathrm{Ba_2Cu_3O_{7-x}}$ where R=La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu.[1-3] All these materials have the same orthorhombic structure with space group *Pmmm* for high oxygen content (x less than about 0.5).[4-6] Investigations of the superconducting phase have shown that the rare-earth ions are triply ionized,[7] raising the possibility of observing transitions between crystal-field levels of the ground configuration. Studies of the crystal-field interaction in high-T_c superconductors by means of electron-spin resonance, specific-heat measurements, and inelastic-neutron scattering have been productive.[8-10] For example, energy levels and crystal-field parameters for the ground J level of Er in $\mathrm{ErBa_2Cu_3O_{7-x}}$ have been determined by neutron scattering.[8]

In this paper we report on an investigation designed to detect optical absorption by the rare-earth ions. The chief advantage of an optical absorption study is the ability to observe many crystal-field levels whose transitions lie in or near the visible region of the spectrum. The main difficulty is the relative opacity of the high-T_c superconductors at visible wavelengths. Using a carefully illuminated grating spectrometer, a diode-array detector and considerable analysis, we have reached signal-to-noise ratios of 10^5. As will be shown in the following, this sensitivity makes it easy to observe crystal-field lines in thin films of rare-earth insulators, as oscillator strengths are typically about 10^{-6} for electric dipole transitions in these materials.[11] In the superconductor, though, the rare-earth site is an approximate center of symmetry, and parity conservation prohibits electric dipole transitions between crystal-field levels of the same configuration. However, magnetic dipole transitions following the selection rules $\Delta S=0$, $\Delta L=0$, and $\Delta J=0,\pm 1$ are allowed. The required proximity in energy implied by these rules usually places the transitions in the infrared, but mixing between ${}^{2S+1}L_J$ levels in intermediate coupling allows transitions to occur in the visible with corresponding oscillator strengths of a few times 10^{-8} (Ref. 11).

II. ABSORPTION IN THIN FILMS

If light travels a distance d through an absorbing film, its intensity is reduced according to the familiar exponential law $I=I_0e^{-\alpha d}$, where α is the absorption coefficient. Assuming the absorption line of interest has a Lorentzian line shape with an oscillator strength f, the relative change in intensity at line center is

$$\frac{\Delta I}{I}\approx\frac{f}{40}\frac{Nd}{\Delta\nu_0}\ , \tag{1}$$

where N is the number of absorbing atoms per cm^3 and $\Delta\nu_0$ is the full linewidth at half maximum.[12] For rare-earth atoms in crystals $\Delta\nu_0$ typically lies in the range 30–300 GHz (1–10 cm^{-1}), and N is about 6×10^{21} cm^{-3} for the high-T_c superconductors.

There is an optimum film thickness which results from the competition between two effects: The signal due to absorption is proportional to the film thickness d, but the signal-to-noise ratio is proportional to the square root of the transmitted intensity, $\sqrt{I_0}e^{-\alpha d/2}$. Maximizing the product $d\times e^{-\alpha d/2}$ gives $d=2/\alpha$, or two skin depths.

As a numerical example, our film of $\mathrm{ErBa_2Cu_3O_{7-x}}$ had a thickness of 3000 Å which was near the optimum value of two skin depths. Taking $\Delta\nu_0$ to be 100 GHz, N about 6×10^{21} cm^{-3}, and d=3000 Å, we find that a sensitivity $\Delta I/I$ of 10^{-5} allows detection of oscillator strengths as small as 2×10^{-10}. Lines broadened due to strains in a poor film could significantly increase this estimate.

III. APPARATUS

The apparatus consists of a white-light source, dewar, grating spectrometer, and photodiode array, arranged as shown in Fig. 1. Use of a grating spectrometer offers the advantage of easy tunability over a wide wavelength range, and a one-meter Czerny-Turner instrument pro-

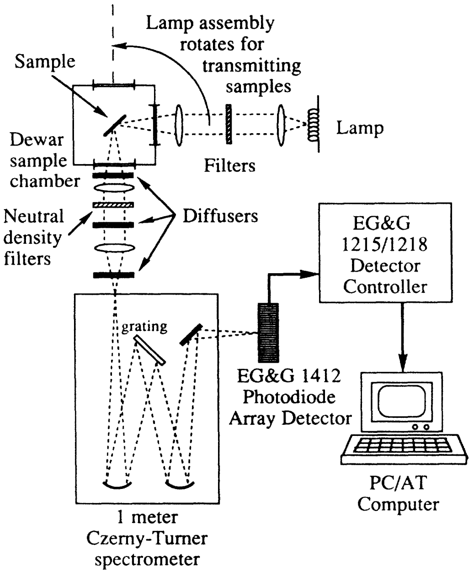

FIG. 1. Experimental apparatus.

vides adequate resolution for all but very narrow transitions. Addition of a photodiode-array detector allows the system to collect an entire spectrum at once, eliminating many sources of noise (such as light-source fluctuation), which can plague scanning systems.

When used to detect very weak absorption, a grating-spectrometer system exhibits several undesirable characteristics which must be dealt with.[13] In order to compensate for slightly unequal photodiode gains it is necessary to compare each data spectrum to a "reference spectrum," taken with no sample in place. Unfortunately, removing the sample has strongly adverse effects on the signal-to-noise ratio, making a good reference spectrum difficult to obtain.

First, remember that to calculate the diffraction pattern of a given aperture illuminated by a uniform plane wave, one takes the Fourier transform of the aperture's transmittance or reflectance function (called the "aperture function" or "pupil function").[14] Normally, a grating's aperture function has one major spatial-frequency component due to the regularly spaced grooves; monochromatic light incident on the grating is therefore diffracted (for a given order) through a very specific angle determined by the grating spacing. If the illumination is nonuniform, then the various grating grooves contribute unequal amounts to the diffracted wave, and we must multiply the aperture function by the illumination function before taking the Fourier transform. This effectively modulates the aperture function and introduces sidebands into the diffraction pattern.

In the present case, the grating illumination is not uniform. Consider the arrangement in Fig. 1. Because the spectrometer entrance slits are narrow (about 40 μm, they act as a pinhole camera in one dimension and image every component in the optical path onto the grating. By removing the back-cover plate from the spectrometer, it is possible to view directly on the grating surface irregularities in illumination due to the coiled tungsten lamp filament and optical stops introduced by the dewar-window edges and small samples. The generation of sidebands means that monochromatic light incident on the grating is not focused onto a single photodiode in the array but is spread over a larger region. Removing the sample to collect a reference spectrum changes the irregular illumination pattern, slightly altering the diffraction sidebands and leading to irregular but reproducible features in the final spectra. We note that the illumination is only slightly nonuniform; these sidebands would not present a problem were we not attempting to achieve such high signal-to-noise ratios. Preparing the reference spectrum to have the same intensity as the data spectrum reduces, but does not eliminate, these effects.

The solution to these difficulties is proper diffusion of the light entering the spectrometer. As far as the spectrometer is concerned, the light passing through the entrance slits should "look the same" for both the data and reference spectra. We have found that a combination of ground glass and acid-etched glass diffusers offers the best performance. The very smooth acid-etched diffusers are placed closest to the entrance slits of the spectrometer. The diffusers remove most of the information about sample displacement, and the result is a reference spectrum indistinguishable from the data spectrum (except, of course, for possible absorption lines) at signal-to-noise ratios up to about 10^5. Unfortunately, the price paid for diffusion is a reduction in light intensity by a factor of 5 or 10, depending on the number of diffusers used and their positions in the optical path. The detector and associated electronics produce very little noise of their own with the result that about 75% of the noise in any given collection interval is due to photon shot noise. Because of this the signal-to-noise ratio obtainable is ultimately limited by the system's light throughput, determined chiefly by the geometric characteristics of the grating spectrometer and the low intrinsic brightness of tungsten-light sources. We have obtained signal-to-noise ratios as high as 10^5 for highly reflecting samples and about 10^4 for the strongly absorbing samples studied here.

IV. EXPERIMENTAL DETAILS

Bulk samples of $R\mathrm{Ba_2Cu_3O_{7-x}}$ with $R=\mathrm{Er}$, Ho, and Yb were made by the methods standard for these materials.[15] The samples of "green phase," $\mathrm{Er_2BaCuO_5}$ and $\mathrm{Yb_2BaCuO_5}$, were prepared in the same manner but sintered at only 800 °C. Before cooling in liquid nitrogen, the samples were scraped to remove a surface layer. They were not polished, as it seemed that working the surface might introduce unwanted strains that would broaden crystal-field lines. The thin film of $\mathrm{ErBa_2Cu_3O_{7-x}}$ was a c-axis-oriented epitaxial film, prepared by evaporation in the presence of oxygen followed by a high-temperature oxygen anneal.[16]

These materials present a problem for the sensitive optical-absorption spectrometer because of their opacity. The skin depth is only about 1000–1500 Å, so a thin film is necessary to study the sample in transmission. Unfortunately, the only thin film we were able to obtain was quite small (about 0.25 cm^2), limiting the amount of light reaching the detector and reducing the signal-to-noise ratio. The other possibility is to study reflection from a large-area bulk sample. This method also has the disadvantage of low light levels, since bulk samples of these materials reflect very little light. The low light levels reduced the signal-to-noise ratio for both types of samples to about 10^4 for a single run.

Spectra were taken at 77, 4, and 2.2 K. Some runs were taken below the λ-point, where liquid helium is transparent, to increase the sharpness of lines and to collect as much light as possible. The 77-K data were useful in obtaining several low-lying states of the ground level of Er^{3+}, $^4I_{15/2}$.

V. RESULTS AND ANALYSIS

A. Erbium

Several levels observed in $ErBa_2Cu_3O_{7-x}$ and Er_2BaCuO_5 are displayed in Fig. 2, along with lines of Er^{3+} in some well-studied crystals. Note that the lines in Er_2BaCuO_5 correspond closely to those in Er_2O_3, particularly for the $^2H_{11/2}$ level. Three spectra at 2.2 and 4.2 K appear in Figs. 3–5, in which the high-T_c film and the bulk green-phase sample can be compared. For compar-

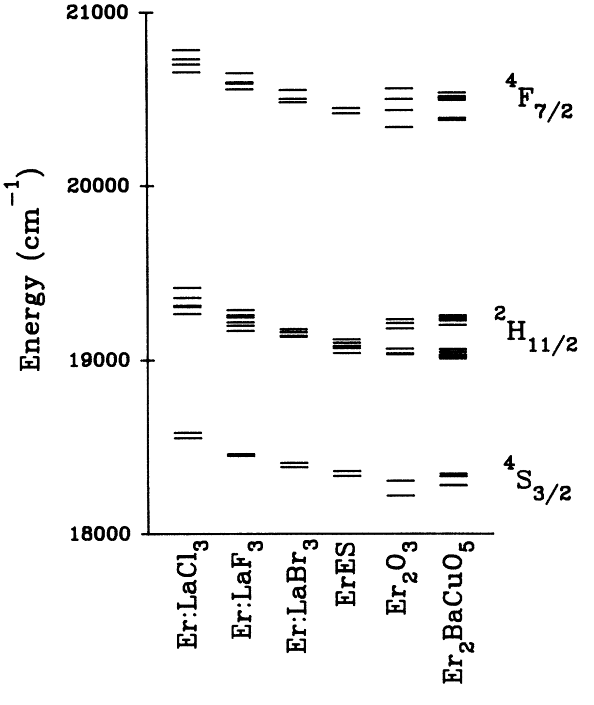

FIG. 2. Energy diagram for several $^{2S+1}L_J$ levels of Er^{3+} in previously studied materials as well as erbium green phase, Er_2BaCuO_5. The $^4F_{7/2}$ level is included for comparison but was too weak to observe in the $ErBa_2Cu_3O_{7-x}$ film. Note the similarity between green-phase and oxide energies. ES stands for ethyl sulfate.

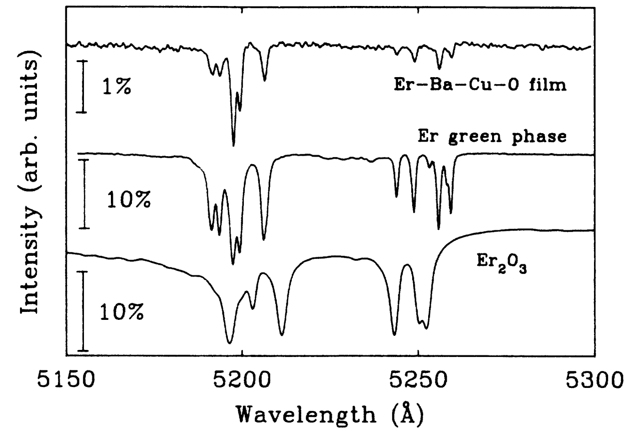

FIG. 3. Spectra of the $^4I_{15/2}\rightarrow{}^2H_{11/2}$ transition in $ErBa_2Cu_3O_{7-x}$, Er_2BaCuO_5, and Er_2O_3 at 4 K. The deepest absorption was 2% in the film and 15% in the green-phase sample.

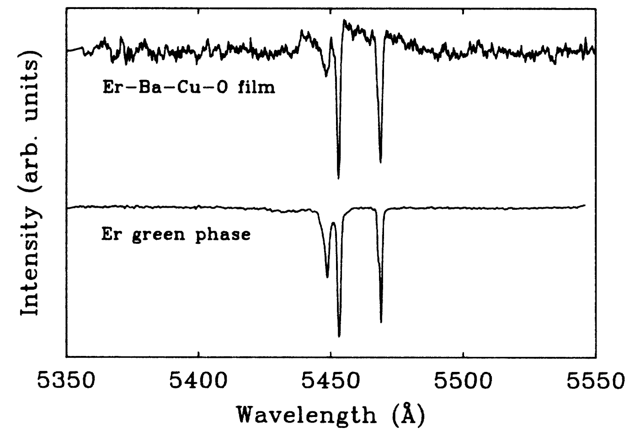

FIG. 4. Spectra of the $^4I_{15/2}\rightarrow{}^4S_{3/2}$ transition in $ErBa_2Cu_3O_{7-x}$ and Er_2BaCuO_5 at 4 K. The deepest absorption was 0.2% in the film and 8% in the green-phase sample.

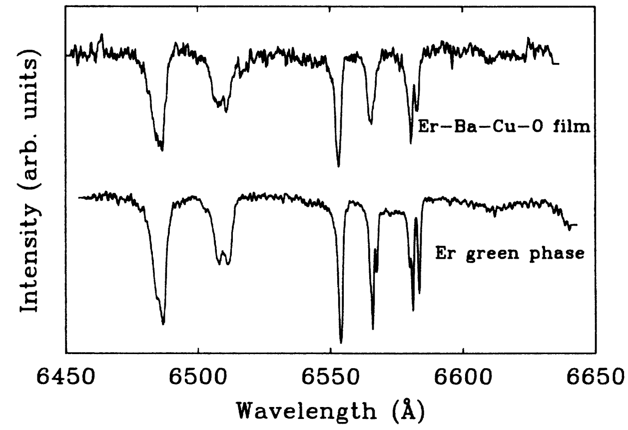

FIG. 5. Spectra of the $^4I_{15/2}\rightarrow{}^4F_{9/2}$ transition in $ErBa_2Cu_3O_{7-x}$ and Er_2BaCuO_5 at 4 K. The deepest absorption was 0.3% in the film and 3% in the green-phase sample.

TABLE I. Estimated oscillator strengths for selected transitions in the $ErBa_2Cu_3O_{7-x}$ film.

Level	Energy (cm^{-1})	$f\times10^6$
$^2H_{11/2}$	19 230	38
	19 013	16
$^4S_{3/2}$	18 280	7
$^4F_{9/2}$	15 191	11

ison Fig. 3 shows the spectrum of Er_2O_3 and the relative amounts of absorption. Note that the reflection spectrum is shown for the oxide and the bulk materials while transmission is more appropriate for the high-T_c film. The lines in the green-phase sample are about ten times stronger than those in the superconductor. The states are Kramers degenerate; thus for each $^{2S+1}L_J$ level we expect a maximum of $(2J+1)/2$ crystal-field lines. However, since there are two distinct crystallographic sites for the rare-earth ion in the green phase,[17] extra lines are visible in the spectra. The excess of lines due to the two sites is most clearly visible in Fig. 5.

By taking spectra at 77 K we were able to detect several thermally excited states of the $^4I_{15/2}$ ground level of Er^{3+} at 41, 72, and 95 cm^{-1}. These values are averages over the two rare-earth sites because the extra lines appearing at 77 K were too broad to resolve the sites individually. Consistent with the similarity in excited levels mentioned above, the states in the ground level are quite close to the corresponding states in Er_2O_3 in which the energies are 39, 76, and 89 cm^{-1}.[18]

Since x-ray studies of the high-T_c film place an upper limit of less than 1% on the amount of green-phase present,[19] the oscillator strengths of the transitions can be estimated. The results for a few of the stronger transitions appear in Table I. The numbers are consistent with electric dipole oscillator strengths of Er^{3+} in other crystals. We note that oscillator strengths obtained from a pure green-phase sample could be used to determine very small green-phase concentrations in high-T_c superconductors. Concentrations more than an order of magnitude smaller, less than 0.1%, would be quite visible.

The strongest magnetic dipole transitions in Er^{3+} involve the excited levels $^4I_{13/2}$ and $^2K_{15/2}$, but these are in the infrared and near ultraviolet, respectively, and outside the range of our detector. We did observe more than the allowed $(2J+1)/2$ lines for each level, but these lines were all much stronger in the green-phase sample and so must be electric dipole transitions due to the impurity phase. We note that very weak lines in the superconductor would be difficult to detect if they lie close to the much stronger green-phase lines. Nevertheless, we estimate using Eq. (1) that if the lines are not significantly broadened, any magnetic dipole oscillator strengths must be considerably smaller than 10^{-8} in order for the lines not to appear in our spectra.

B. Holmium

In an attempt to observe transitions due to the superconductor rather than the impurity phase, we examined a pellet of $HoBa_2Cu_3O_{7-x}$. The ground level of Ho^{3+}, denoted in the *LS* basis as $^5I_8$, contains about 4% $^3K_8$ according to intermediate coupling calculations.[20] This allows a magnetic dipole transition to occur between the (*LS*) levels $^5I_8$ and $^3K_8$. In fact, this is one of the strongest visible magnetic dipole transitions in any of the 3+ lanthanides, having a predicted oscillator strength of about 6×10^{-8} for ions in solution.[11] Assuming a reasonable linewidth, Eq. (1) predicts an absorption of about 0.05% from a transition in the superconductor. Although the low light level reflected by the sample reduced our signal-to-noise ratio to about 10^4, this is clearly sufficient to detect such a magnetic dipole transition.

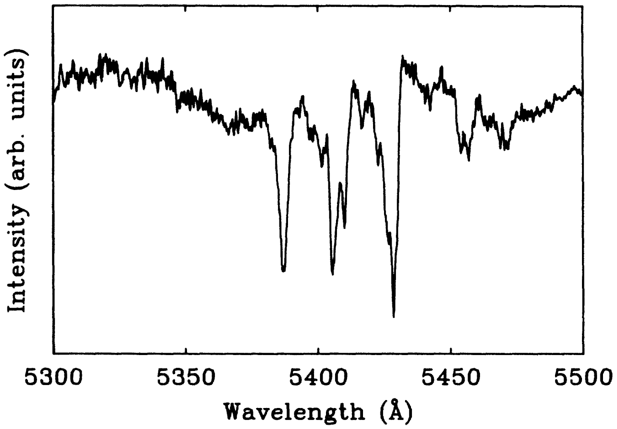

FIG. 6. Spectrum of the $^5I_8\rightarrow{}^5F_4$ transition in $HoBa_2Cu_3O_{7-x}$ bulk material at 4 K. The deepest absorption was 0.09%.

Despite these arguments, no evidence of this magnetic dipole transition was found in the $HoBa_2Cu_3O_{7-x}$ sample. The observed lines in $HoBa_2Cu_3O_{7-x}$ are electric dipole transitions corresponding to the $^5F_4$ level, and a number of very weak transitions associated with the $^5F_3$, $^5F_2$, and $^5G_6$ levels. Figure 6 shows the spectrum of the $^5F_4$ level. These spectra cover the energy range 18 500–22 000 cm^{-1}. We assume that these lines are due to the impurity phase Ho_2BaCuO_5, as was the case in $ErBa_2Cu_3O_{7-x}$; no impurity-rich sample was available for holmium. No lines were found in the region around 21 500 cm^{-1}, the usual location for the $^3K_8$ level. Indeed, all the lines in the entire region are most easily attributed to electric dipole transitions in the green phase. We conclude that either the oscillator strength for the $^5I_8\rightarrow{}^3K_8$ transition in the superconductor is unusually small or the lines are broadened by strain or by conduction-electron effects.

C. Ytterbium

The transition in Yb^{3+} between the ground level, $^2F_{7/2}$, and the first excited level, $^2F_{5/2}$, is the strongest magnetic dipole transition within the range of our detector in any of the triply-ionized rare earths, having an oscillator strength of 17.8×10^{-8} for ions in solution.[11]

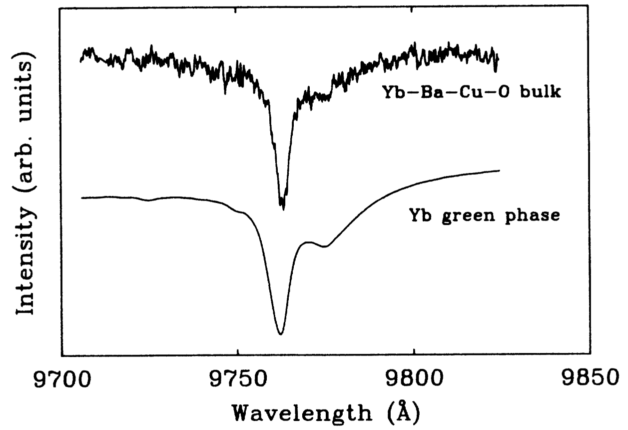

FIG. 7. Spectra of the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition in $YbBa_2Cu_3O_{7-x}$ and Yb_2BaCuO_5 at 4 K. The deepest absorption was 0.8% in the superconductor and 10% in the green-phase sample.

This is nearly three times that of the $^5I_8\rightarrow{}^3K_8$ transition in Ho^{3+} because the transition is magnetic-dipole allowed; we need not rely on mixing due to intermediate coupling. The $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition occurs at about 10 000 cm^{-1}, near the low-energy limit of our detector, but the increase in oscillator strength more than compensates for the decrease in signal.

Two samples were prepared, $YbBa_2Cu_3O_{7-x}$ and Yb_2BaCuO_5. Once again, the lines observed in the high-T_c material are due to green-phase impurities. Two of the expected three lines from this level were observed, at energies consistent with Yb lines in other crystals. Clear evidence of the two rare-earth sites in the green phase is visible in Fig. 7, which shows the low-energy component of the $^2F_{5/2}$ level. Another component near 10 500 cm^{-1} is very broad and could easily hide a weak nearby line. The scans were taken over the energy range 10 000–10 700 cm^{-1}.

VI. CONCLUSIONS

The absence of sharp absorption lines in the superconducting phase may well be due to a combination of broadening and proximity to the much stronger green-phase lines. As Fig. 3 shows, the lines in Er_2O_3 overlap the green-phase lines in the high-T_c film. If weak broad lines in the superconductor also lie in this region, they would be very difficult to identify. In addition, the presence of two rare-earth sites in the green phase often leads to a multiplicity of closely spaced lines. However, previous studies have shown that the crystal electric fields in the superconductors are comparatively large, reducing the likelihood of overlap. In any case, a sample free of the green phase would make identification of possible transitions in the superconductors much easier.

The problem of green-phase contamination occurs in samples prepared in very different ways. In the evaporated thin film and the bulk sintered materials, the impurity is present in clearly visible amounts. Studies indicate that various impurities and defects affect the superconductor's critical-current density and flux-pinning properties.[21] This method provides a very sensitive probe of impurities in these materials.

In closing, we have demonstrated a very sensitive technique for observing weak absorption lines by measuring reflected or transmitted intensities to one part in 10^5 or more. Impurity concentrations of about 1% green phase were observed in both bulk and thin-film samples of high-T_c superconductors, and the technique could easily identify concentrations on the order of 0.1%. The method should prove useful in studying impurity-dependent characteristics of these materials, and may reveal in a pure sample absorption lines due to transitions in the superconductor itself.

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