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# Laser heating of a sintered oxide superconductor

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Raman spectroscopy, in which a laser beam serves the dual role of exciting the Raman spectrum and annealing the sample, shows promise as a means of investigating oxygen effects in the oxide superconductors. A technique is described, based on measurements of the ratios of the areas of corresponding peaks in the anti-Stokes and Stokes spectra, whereby the temperature of the illuminated region of the sample can be determined as a function of the power in the incident laser beam. It is found that, for sintered samples of bismuth 2122, a small correction must be made for the departure from thermodynamic equilibrium induced by the pumping effect of the laser beam.

## I. INTRODUCTION

The properties of the oxide superconductors prove to be very sensitive to oxygenation. Whether a compound is annealed in air, or in oxygen, or in an oxygen-free environment, and how rapidly it is heated and cooled, can determine whether or not it superconducts.<sup>1,2</sup> In developing stable materials, the possibility of degradation by exchange of oxygen with the environment must also be considered. Raman spectroscopy, in which a laser beam serves the dual role of exciting the Raman spectrum and annealing the sample, shows promise as a means of investigating oxygen effects in the oxide superconductors.

When the surface of an oxide superconductor is illuminated by electromagnetic radiation of photon energy  $\hbar\omega$ , the spectrum of scattered light is dominated by a strong elastic peak known as the *Rayleigh peak*. In addition, a weak inelastic scattering spectrum known as the *Raman spectrum* is observed on either side of the Rayleigh peak. The individual peaks of the Raman spectrum represent the dynamic modulation of the dielectric function of the sample by its various normal modes of vibration. To each normal mode of frequency  $\Omega$  there correspond two Raman peaks, which are shifted in frequency by  $\pm\Omega$  with respect to the Rayleigh peak. The peaks shifted to lower energy constitute the *Stokes* spectrum, while the peaks shifted to higher energy constitute the *anti-Stokes* spectrum. The frequency shift  $\Omega$  is termed the *Raman shift*.

Those normal modes of the oxide superconductors that are dominated by the motions of oxygen atoms are associated with large Raman shifts, and the peak strengths, while weak, are readily measured. Moreover, oxygen atoms in inequivalent lattice sites yield well-separated Raman peaks. The laser-induced temperature rise is highly localized but essentially uniform over the illuminated area, the thermal time constant is short, and the composition and pressure of the ambient gas can be easily controlled.

Unfortunately, it is not easy to measure the temperature rise of the illuminated region of a laser-illuminated sample by conventional means. The purpose of the present paper is to describe a technique, based on a measurement of the ratio of the areas of corresponding peaks in the anti-Stokes and Stokes spectra, whereby the laser-induced temperature rise of the illuminated region of the sample can be determined as a function of the power in the incident laser beam. Similar techniques have previously been applied to determine the temperature rise of laser-illuminated semiconductors.<sup>3</sup> It is shown that, in the materials discussed here, the pumping effect of the laser beam induces a small but significant departure from thermodynamic equilibrium.

## II. SAMPLE PREPARATION

Our samples are high-density, high-purity, sintered oxide superconductors of nominal composition  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$ , commonly known as bismuth 2122.<sup>4</sup> They were prepared by a conventional solid-state reaction technique, starting from  $\text{BaO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$ , each of purity 99.995%. The starting materials were machine ground for 2 h, then calcined at 800 °C for 12 h. The calcined powders were reground for 2 h and then sintered at 870 °C for 24 h. The sintered materials were reground for 2 h, pelletized, annealed in air for 80 h at 860 °C, and furnace cooled to room temperature.

The Stokes and anti-Stokes spectra of a typical sample of bismuth 2122 are shown in Fig. 1. Three prominent peaks are observed, at Raman shifts of approximately  $\pm 300$ ,  $\pm 470$ , and  $\pm 640 \text{ cm}^{-1}$ . It is generally accepted on the basis of lattice dynamical calculations and other evidence that these three peaks are attributable to normal modes of the lattice that are dominated by vibrations of the oxygen atoms in the copper, strontium, and bismuth layers, respectively.

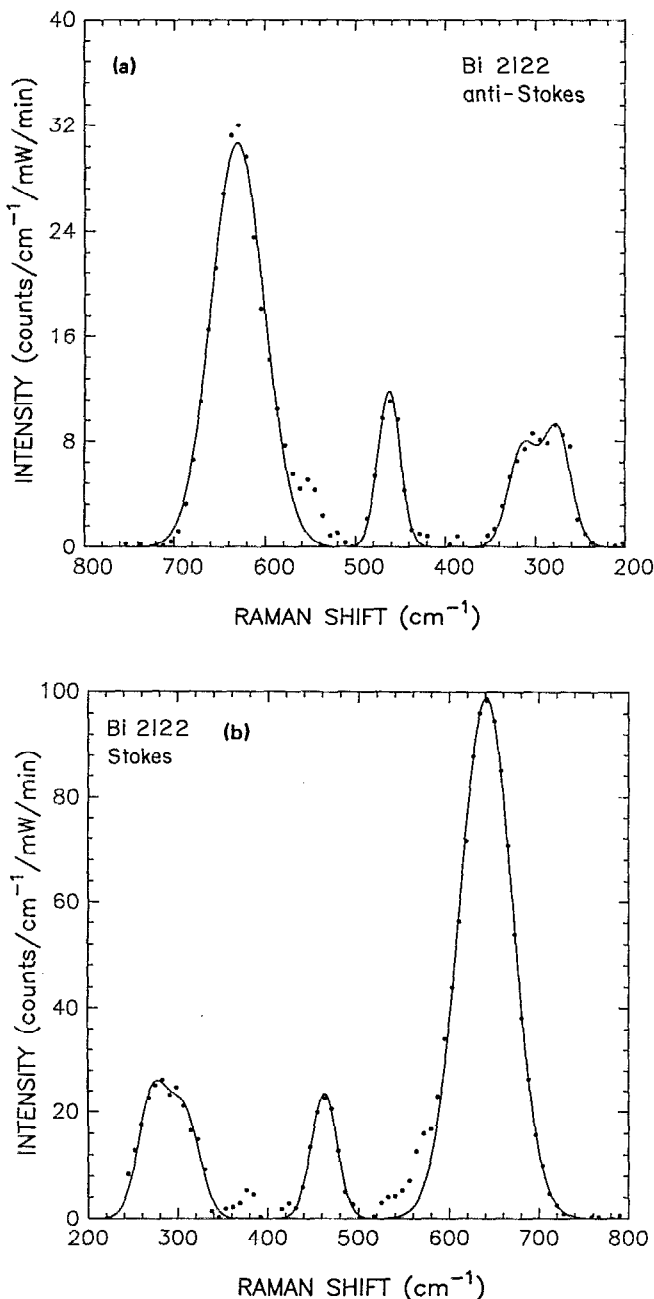


FIG. 1. Anti-Stokes and Stokes Raman spectra of a sintered sample of Bi 2122 after annealing at 550 °C in dry nitrogen gas. The surface is illuminated by a focused argon ion laser operating at 514 nm. The power in the focal spot is approximately 28 mW.

It is known that, whereas the cation structure of bismuth 2122 undergoes no gross change up to the melting temperature, some oxygen can be removed by annealing the sample at relatively low temperature. Loss of oxygen may contribute an anomalous temperature dependence to the strengths of the Raman peaks, making it impossible accurately to compare the strengths of the Stokes and anti-Stokes peaks unless the spectra are recorded simultaneously. As we are not able to record the two spectra simultaneously, our samples were annealed in a flow of dry nitrogen gas for 24 h at 550 °C in an attempt to stabilize the

oxygen content. The zero-resistance temperature of the resulting samples is 94 K, and the width of the onset of resistance is approximately 4 K.<sup>5</sup> Scanning electron micrographs reveal the presence of voids with a total area of approximately 10% of the area of each sample, as well as small inclusions of a bismuth-deficient dark phase with a total area of less than 2%. The grain size is in the range 1 to 5  $\mu\text{m}$ .

### III. DETERMINATION OF THE SAMPLE TEMPERATURE

The Raman spectrum results from indirect transitions between the ground state of the sample and low-lying excited states at energies  $\hbar\Omega$ . The transitions involve real or virtual intermediate states of energy close to  $\hbar\omega$ , the energy of the incident photons. The elementary theory of the Raman effect<sup>6,7</sup> shows that the relative strength of anti-Stokes and Stokes transitions, expressed as the ratio of the areas beneath the corresponding peaks, is given by

$$A_a/A_s = n_1/n_0, \quad (1)$$

where  $n_1/n_0$  is the ratio of the population of the excited state to the population of the ground state. For a sample in thermodynamic equilibrium, the ratio of the population of the excited state to the population of the ground state is given by the Boltzmann factor, and therefore

$$A_a/A_s = \exp(-\hbar\Omega/k_B T). \quad (2)$$

It follows that, for a sample in thermodynamic equilibrium, careful measurements of the strengths of corresponding peaks in the anti-Stokes and Stokes spectrum can be used to determine the temperature of the illuminated region of the sample.

As the oxide superconductors are strong absorbers of visible light, illuminating a sample not only increases the temperature of its constituent crystallites, but also modifies the occupation of the various excited states. If the distribution over excited states differs significantly from a Boltzmann distribution, then the derivation of Eq. (2) is no longer valid, and a more complete analysis is needed to extract the temperature of the sample.

In an illuminated sample, the relative population of a low-lying excited state can be deduced from a simple rate-equation analysis. It is convenient to adopt the total power  $P$  emitted by the laser as a measure of the intensity of illumination at the surface of the sample. Let  $k_u$  and  $k_d$  represent the rate constants for upward and downward transitions between the ground state and the low-lying excited state of energy  $\hbar\Omega$ , and let  $\sigma P$  be the rate of radiation-induced transitions to the intermediate states of energy  $\hbar\omega$ . Then it is easy to show that the relative population of the low-lying excited state is given by

$$\frac{n_1}{n_0} = \frac{k_u + \sigma P}{k_d + \sigma P}. \quad (3)$$

In the limit of small  $P$ , the expression for  $(n_1/n_0)$  must reduce to the Boltzmann factor. It follows that

$$\frac{n_1}{n_0} = \frac{\exp(-\hbar\Omega/k_B T) + (\sigma/k_d)P}{1 + (\sigma/k_d)P} \quad (4)$$

Thus, so long as the value of the pumping parameter  $\sigma/k_d$  is known, the temperature of the sample can be determined as a function of the power in the laser beam by fitting the ratio of the areas of corresponding peaks in the anti-Stokes and Stokes spectra to an expression of the form of Eq. (4).

Raman measurements have been used to establish the relationship between temperature and laser power for sintered samples of the oxide superconductor bismuth 2122. The samples were illuminated by the focused beam of an argon ion laser operating at 514 nm. The power in the laser beam was increased in steps to a maximum well below the power needed to melt the surface of the sample, then decreased in steps to zero. At each step, the Raman spectrum was recorded. After background subtraction, the areas of corresponding Stokes and anti-Stokes peaks were determined by fitting with functions of Gaussian form.

As the  $640\text{-cm}^{-1}$  peak is by far the strongest peak, its area can be measured with the greatest precision. Moreover, as it has the largest Raman shift, its strength is inherently the most sensitive to temperature. For these reasons the  $640\text{-cm}^{-1}$  peak yields by far the most accurate temperatures. From the  $640\text{-cm}^{-1}$  peak, unlike the other peaks, consistent ratios of areas were obtained only on the second and subsequent cycles of laser annealing. It is believed that the oxygen content of the bismuth layers was stabilized by the first cycle of laser annealing; prior annealing in dry nitrogen gas was not sufficient.

A least-squares fitting procedure has been developed to interpret the data. It was assumed that  $\sigma/k_d$  is independent of temperature and laser power, and that the relationship between temperature and laser power can be represented with sufficient accuracy by a quadratic expression of the form

$$T = T_a + a_1 P + a_2 P^2, \quad (5)$$

where  $T_a$  is the ambient temperature. For a range of values of  $\sigma/k_d$ , the temperature of the illuminated region of the sample was calculated by interpreting the measured ratio of the areas of corresponding anti-Stokes and Stokes peaks on the basis of Eqs. (1) and (4). Then the coefficients  $a_1$  and  $a_2$  in Eq. (5) were adjusted to yield the best fit to the calculated temperature expressed as a function of the laser power. It was found that the quality of the fit is essentially independent of  $\sigma/k_d$ .

The value of the pumping-parameter  $\sigma/k_d$  was determined by measuring the minimum laser power required to melt the surface of the sample. In the Raman spectrometer, a magnified image of the sample surface is formed at the first grating. As the power in the laser beam is increased, a transition is observed from a static image to an image in vigorous motion. The transition, which is sharp and reversible, is interpreted as being due to the melting of the surface of the sample. Care must be taken in measuring the melting power for, if the critical beam power is greatly exceeded, the image of the surface becomes defocused, and

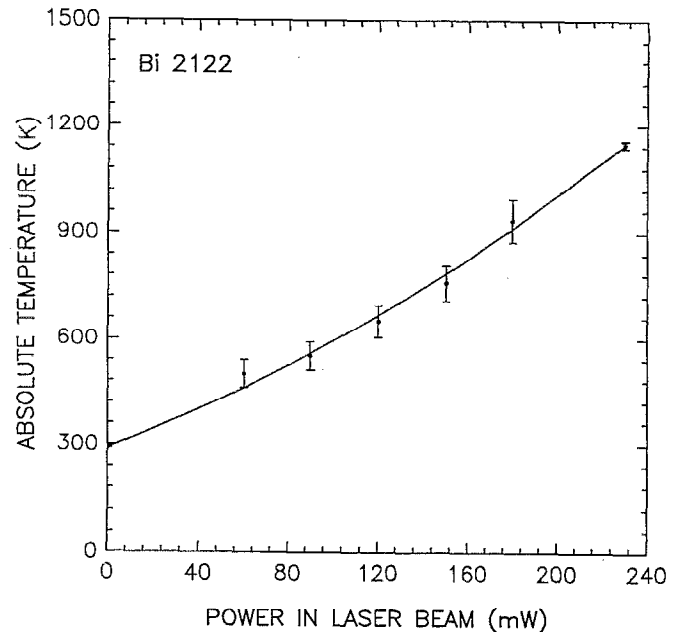


FIG. 2. Best quadratic fit to the temperature of the illuminated region of the surface deduced from the ratio of areas of anti-Stokes and Stokes peaks, plotted as a function of the laser power. The power in the focal spot is  $\approx 0.19$  times the laser power. The coefficients have been selected to fit the curve to the experimentally-observed melting power and melting temperature (230 mW, 875 °C).

the transition proves to be no longer reproducible. This is believed to indicate the formation of a cavity in the surface of the sample as a result of melting over an extended volume.

Knowing the minimum laser power that is required to melt the surface of the sample, the melting temperature of the illuminated region of the sample can be calculated from Eq. (5). The calculated melting temperature is found to vary significantly with the value of  $\sigma/k_d$  that was assumed in determining the coefficients  $a_1$  and  $a_2$ . Hence  $\sigma/k_d$  can be determined by finding the value that brings the calculated melting temperature into agreement with the melting temperature obtained from a direct measurement on a bulk sample,  $T_m = (875 \pm 10)^\circ\text{C}$ . The result is

$$\sigma/k_d = (8.4 \pm 2.6) \times 10^{-5} \text{ mW}^{-1}. \quad (6)$$

Our best quadratic fit to the dependence of the temperature of the illuminated region of the sample on the laser power, with  $a_1 = 2.49 \text{ K} \cdot \text{mW}^{-1}$  and  $a_2 = 0.0054 \text{ K} \cdot \text{mW}^{-2}$ , is shown in Fig. 2.

For the materials discussed here, and assuming a melting power of 230 mW, the pumping correction to the total transition rate is at most about 2%. A calculation in which the laser-induced departure from thermodynamic equilibrium is neglected overestimates the temperature at the melting power by about 30 K. Hence in determining the temperature of a sample of bismuth 2122 from the ratio of the areas of corresponding anti-Stokes and Stokes peaks, the correction for the laser-induced departure from thermodynamic equilibrium is small but significant.

There is no reason to suppose that the pumping parameter is rigorously independent of the intensity of illumination as assumed above, although no such dependence need be invoked to account satisfactorily for the data. In order to check whether the data might alternatively be consistent with a pumping parameter that depends on intensity of illumination (or temperature), a further least-squares fit was made in which  $\sigma/k_d$  was assumed to depend on beam power as

$$\sigma/k_d = b_1 + b_2 P, \quad (7)$$

and in which the relationship between  $T$  and  $P$  was represented by the linear expression

$$T = T_a + a_1 P. \quad (8)$$

This linear model yielded a much poorer fit to the data than the quadratic model presented above, and no set of parameters was found to bring the predicted temperature at the melting power into agreement with the experimental result. A quadratic term in the relationship between  $T$  and  $P$  appears to be essential for a satisfactory fit to the data.

If it is assumed that the thermal conductivity of the oxide superconductor is a linear function of temperature, then it is straight-forward to solve the equation of thermal conduction and relate the coefficients in Eq. (5) to the transport properties of the sample. It is found that the logarithmic derivative with respect to temperature of the thermal conductivity  $\kappa$  is given by

$$\frac{d(\ln \kappa)}{dT} = - [(a_1^2/4a_2) + T_a]^{-1}. \quad (9)$$

Hence the temperature derivative of the thermal conductivity of the oxide superconductor can be estimated from the best set of fitting coefficients. For sintered samples of bismuth 2122 the result is

$$\frac{d(\ln \kappa)}{dT} = - 0.0017 \text{ K}^{-1}. \quad (10)$$

The consistency of this result with data for similar materials [for example CuO, for which  $d(\ln \kappa)/dT \approx -0.002 \text{ K}^{-1}$  over a similar temperature range] suggests that the temperature dependence of the thermal conductivity of the sample is primarily responsible for the quadratic term in the relationship between laser power and temperature.

#### IV. CONCLUSIONS

The technique reported here, based on measuring the ratio of the areas of corresponding anti-Stokes and Stokes peaks in the Raman spectrum, accurately determines the linear and quadratic terms in the relationship between the temperature in the illuminated region of the surface of an oxide superconductor and the power in the incident laser beam. For sintered samples of bismuth 2122, a small correction must be made for the departure from thermodynamic equilibrium induced by the pumping effect of the laser beam. The quadratic term apparently arises from the temperature dependence of the thermal conductivity. This technique is the basis of an ongoing investigation of oxygen effects in the oxide superconductors, the results of which will be reported elsewhere.

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