## Anomalous Raman spectra from La<sub>2</sub>CuO<sub>4</sub>

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We show that some published Raman spectra from the superconductors  $(La_{2-x}Sr_x)CuO_4$  and  $La_2NiO_4$  are incorrect. We believe that these spectra were obtained when the samples were "burnt" by the focused laser beam and were actually due to  $La_2O_3$ . Similar anomalous results can be obtained when starting with Nd<sub>2</sub>CuO<sub>4</sub> where the spectra come from Nd<sub>2</sub>O<sub>3</sub>. A spectrum distinctly different from those of  $La_2O_3$  or Nd<sub>2</sub>O<sub>3</sub> is obtained from Y<sub>2</sub>O<sub>3</sub>.

Blumenroeder et al.<sup>1</sup> have reported a three-mode Raman spectrum from  $(La_{2-x}Sr_x)CuO_4$ , the high- $T_c$  material. Their spectrum is more intense, with different frequencies, than other recent measurements on single crystals<sup>2</sup> of this same material. A weaker spectrum with similar frequencies to Blumenroeder et al.<sup>1</sup> has more recently been reported by Ogita et al.<sup>3</sup> in La<sub>2</sub>NiO<sub>4</sub>. This latter material and  $(La_{2-x}Sr_x)CuO_4$  have the so-called T structure.<sup>4</sup> Blumenroeder et al.'s intense spectrum has been of concern in the understanding of these materials.<sup>5,6</sup> On occasion, we have also observed similar Raman spectra from  $(Nd_{2-x}Ce_x)CuO_4$  (unpublished data), the electrondoped superconductor which has the related T' structure.<sup>4</sup> In this paper we explain the origin of these anomalous results.

One result from the structural differences between the T and T' structures is the symmetry of the allowed Raman modes. Group theory predicts the following allowed Raman modes:<sup>7</sup>

- T structure,  $2A_{1g} + 2E_g$ ,
- T' structure,  $A_{1g} + B_{1g} + 2E_g$ .

We ignore the  $2E_g$  modes in the following discussion since usually they are too weak to be observed<sup>2</sup> and when they are observed<sup>2(b)</sup> in isostructural Sr<sub>2</sub>TiO<sub>4</sub>, they are less intense than the  $A_{1g}$  modes. Thus for both of these structures, for Raman modes with atoms vibrating along the c axis, only two modes are expected,  $2A_{1g}$  for materials with the T structure and  $A_{1g} + B_{1g}$  for materials with the T' structure.

In attempting to study the Raman spectra of  $(La_{2-x}Sr_x)CuO_4$ ,  $(Nd_{2-x}Ce_x)CuO_4$ , and their superconducting-metal phases doped respectively with  $Sr^{2+}$ and  $Ce^{4+}$ , we have found that the signals from ceramics are very weak. In fact, we could only be certain of the spectra from single crystals<sup>2,8</sup> when the input laser and output signal were both polarized parallel to the *c* axis. In some ceramics, weak Raman lines could be detected in agreement with our single-crystal results; however, we were not confident of the validity of these weak signals without the polarized-light single-crystal results. Thus, the reported<sup>1</sup> three-line spectrum seemed to us not only too intense, but it contained too many lines.

In attempts to measure the Raman spectra of doped and pure  $(La_{2-x}Sr_x)CuO_4$  and  $(Nd_{2-x}Ce_x)CuO_4$  ceramics, we increased the laser power and shaped the focus. Often this led to an intense Raman spectrum which we called "burn spectra" because microscopic observation showed that we have burned a small hole in the sample at the spot where the laser was focused. Such a burn spectrum is shown in Fig. 1(a). The intensity is about 10 times stronger than the best Raman spectra that we observe in ceramic  $(La_{2-x}Sr_x)CuO_4$  or  $(Nd_{2-x}Ce_x)CuO_4$ . Eventually, it occurred to us that these burn spectra are the same as those published previously.<sup>1,3</sup>

It was easy to determine what materials led to the burn spectra. Figure 1(b) shows the intense Raman spectrum of powdered La<sub>2</sub>O<sub>3</sub>; that of Nd<sub>2</sub>O<sub>3</sub> (not shown) is very similar. Note that the observed signal is about 100 times that of the burn spectra in Fig. 1(a). The frequencies of these intense features are listed in Table I. Thus, a small amount of La<sub>2</sub>O<sub>3</sub> (or Nd<sub>2</sub>O<sub>3</sub>) easily accounts for the reported anomalous spectra.<sup>1,3</sup> The frequencies (Table I) and intensity agree with the burn spectra [Fig. 1(a)] as well as those spectra published earlier.<sup>1,3</sup> For comparison purposes, in Fig. 2 we show the correct Raman spectrum<sup>2</sup> from a single crystal of  $(La_{2-x}Sr_x)CuO_4$ . Although weak in comparison to the spectrum in Fig. 1(a), the  $2A_{1g}$ modes can be clearly seen.

TABLE I. The frequencies (in cm<sup>-1</sup>) of various materials discussed in the text.

| La <sub>2</sub> CuO <sub>4</sub><br>(Ref. 1) | $La_2NiO_4$ (Ref. 3) | La <sub>2</sub> CuO <sub>4</sub><br>(Burn spectra) | Nd <sub>2</sub> CuO <sub>4</sub><br>(Burn spectra) | La <sub>2</sub> O <sub>3</sub> | Nd <sub>2</sub> O <sub>3</sub> | $(La_{2-x}Sr_{x})CuO_{4}$ |
|--|----------------------|--|--|--------------------------------|--------------------------------|---------------------------|
| 98   | 100                  | 99   | 101  | 104                            | 106                            |                           |
| 170  |                      | 182  | 180  | 191                            | 191                            | 226                       |
| 386  | 405                  | 396  | 422  | 411                            | 440                            | 433                       |



FIG. 1. (a) The "burn spectra" that can be observed in Raman measurements of  $La_2CuO_4$  if the laser power is too intense; (b) Raman spectra from  $La_2O_3$ . (The weak feature at 77 cm<sup>-1</sup> is a plasma line.)



FIG. 2. The Raman spectra from single-crystal  $(La_{2-x}-Sr_x)CuO_4$  showing the  $2A_{1g}$  modes. For the x=0 material at room temperature, we also observe the soft mode (associated with the tetragonal-orthorhombic transition) at 93 cm<sup>-1</sup>.

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FIG. 3. Raman spectra from ceramic Y<sub>2</sub>O<sub>3</sub>.

La<sub>2</sub>O<sub>3</sub> (and Nd<sub>2</sub>O<sub>3</sub>) is hexagonal, space group  $D_{3d}^3$  ( $P\overline{3}m1$ ), with one molecule per unit cell.<sup>9</sup> The phonons can be classified according to the

$$2A_{1g} + 3A_{2u} + 2E_g + 3E_u$$

irreducible representations of the  $D_{3d}$  ( $\bar{3}m$ ) point group. Then there should be  $2A_{2u} + 2E_u$  infrared-active phonons and  $2A_{1g} + 2E_g$  Raman-active phonons. We only observe three Raman-active modes from ceramic samples. The same three modes were observed from arc-melted La<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> and we could not detect the fourth expected mode.

The closely related material  $Y_2O_3$ , also used extensively in making many high- $T_c$  material, has a different crystal structure from that of La<sub>2</sub>O<sub>3</sub>.  $Y_2O_3$  has the cubic bixbyite crystal structure<sup>9</sup> with Z = 16 in the body-centered space group  $T_h^7$  (Ia3). Thus, it has 120 normal modes, although many may be degenerate. The Raman spectra are shown in Fig. 3 (that of Ho<sub>2</sub>O<sub>3</sub> is similar). It is very intense and quite different from that of La<sub>2</sub>O<sub>3</sub> or Nd<sub>2</sub>O<sub>3</sub> [Fig. 1(b)]. With the strong narrow mode at 382 cm<sup>-1</sup>, it should be relatively easy to detect as an impurity.

In conclusion, we have shown that some of the reported Raman spectra<sup>1,3</sup> for  $(La_{2-x}Sr_4)CuO_4$  and  $La_2NiO_4$  actually are due to locally decomposed material. The spectra shown are due to  $La_2O_3$ . Similar burn spectra can be obtained if Nd<sub>2</sub>CuO<sub>4</sub> is overheated, then the spectra are due to Nd<sub>2</sub>O<sub>3</sub>.

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