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Raman study of CuO single crystals

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Raman scattering in single-crystalline CuO samples has been studied. From the polarization dependence, the symmetries of the three Raman-active optical phonons have been identified. The A_g Raman mode with frequency of 290 cm^{-1} was found to be strongly polarized along one of the crystal axes. This suggests that there are cancellations between different components of its Raman tensor.

INTRODUCTION

Copper is known to form two oxides, Cu_2O and CuO, which are both semiconductors. As a result of interest in superconducting oxides of Cu, there is now growing interest in the oxides of copper. In particular, CuO resembles some of the superconducting copper oxides in that its crystal structure contains distorted octahedrons with Cu atoms at the center.[1,2] Raman scattering in powders of CuO has been studied by Rosen *et al.*[3] and by Chrzanowski and Irwin.[4] Since polycrystalline samples were used in these studies, the symmetry of the Raman modes could not be determined unambiguously. In this paper we report the results of a study of the polarization dependence of Raman scattering of the three Raman-active optical phonons in CuO. Our results suggest that there are cancellations between the various components of the Raman tensors of some of these modes. As a consequence, the A_g Raman mode is strongly polarized along one axis of the crystal.

RAMAN TENSORS OF PHONON MODES IN CuO

CuO crystallizes in a monoclinic lattice, with two molecules per primitive cell and a space-group symmetry of C_{2h}^6.[1,2] As shown by Chrzanowski and Irwin,[4] there are nine zone-center optical-phonon modes with symmetries $4A_u+5B_u+A_g+2B_g$. Only the even-parity A_g and two B_g modes are Raman active. The forms of the Raman tensors in crystals with C_{2h} symmetry have been listed by Loudon.[5] For the B_g and A_g modes in CuO they are

$$A_g:\begin{pmatrix} a & 0 & d\\ 0 & b & 0\\ d & 0 & c\end{pmatrix},\quad B_g:\begin{pmatrix} 0 & e & 0\\ e & 0 & f\\ 0 & f & 0\end{pmatrix}$$

when referred to a coordinate system (X,Y,Z) where the Y axis is parallel to the twofold rotational axis (same as the primitive translation vector labeled as **b** in Ref. 1). Considering that the orientations of the sample surfaces to be studied are parallel to the [110] and [1$\bar{1}$0] directions, we will introduce another coordinate system: $(X'Y'Z')$ where the X', Y', and Z' axes are oriented along the [110], [1$\bar{1}$0], and [001] directions, respectively. In this new coordinate system the Raman tensors are

$$A_g:\begin{pmatrix} \frac{a+b}{2} & \frac{a-b}{2} & \frac{d}{\sqrt{2}}\\ \frac{a-b}{2} & \frac{a+b}{2} & \frac{d}{\sqrt{2}}\\ \frac{d}{\sqrt{2}} & \frac{d}{\sqrt{2}} & c\end{pmatrix},\quad B_g:\begin{pmatrix} e & 0 & \frac{f}{\sqrt{2}}\\ 0 & -e & \frac{-f}{\sqrt{2}}\\ \frac{f}{\sqrt{2}} & \frac{-f}{\sqrt{2}} & 0\end{pmatrix}.$$

EXPERIMENTAL DETAILS

Experiments have been performed on single crystals of CuO grown from a melt in two different laboratories, using two different techniques. The first batch of samples was grown at the Laboratoire de Chimie du Solide du CNRS in Talence, France. The CuO crystals were byproducts in the growth of single crystals of $YBa_2Cu_3O_{7-\delta}$. The second batch of CuO crystals were grown at Berkeley using the technique described in Ref. 6, from a melt of CuO (99.994), MoO_3 (99.74), V_2O_5 (99.994), and K_2CO_3 (99.9994) in a platinum crucible.

The sample chosen for our experiment from the French batch (to be referred to as sample *A*) was about 3.5 mm long and about 0.5 mm across. The sample showed steps and grain boundaries. However, smooth and optically flat regions indicative of single-crystalline domains of several hundred micrometers across could easily be found on the sample. The sample grown at Berkeley (to be referred to as sample *B*) is smaller, being ~3 mm long and 0.3 mm across. The longer surfaces of sample *B* are very flat and mirrorlike, suggesting that these are cleavage surfaces. In both samples, the cross sections of the sample when viewed from the end are parallelograms. The acute angle of the parallelogram in sample *B* was determined to be approximately 77°. It was pointed out in Ref. 3 that CuO cleaves along the [110] and [1$\bar{1}$0] directions (our choice of axes are identical to those of Ref. 1), and the acute angle between these two cleavage faces should be 72.47°. Thus we conclude that the surfaces of sample *B* are consistent with the identification that they are the [110] and [1$\bar{1}$0] cleavage faces. Since sample *B* has higher quality surfaces and known orientation, more complete polarized Raman studies have been performed on this sample.

The Raman spectra have been excited in a backscattering geometry with an Ar ion laser. Sample *A* shows a broad photoluminescence peak centered at 2.28 eV with a full width at half maxima (FWHM) of 47 meV. Since this luminescence feature is absent in sample *B*, we have assumed that it is associated with defects or impurities in sample *A*. To minimize this luminescence background, the Raman spectra have been excited by the 476-nm line of the Ar ion laser. The scattered radiation was detected with a conventional Spex double monochromator, cooled photomultiplier tube, and photon-counting electronics.

The samples have also been characterized by their reflectivity spectra between 1.5–3 eV. The reflectivity spectra were found to be featureless, except for a monotonic increase in reflectivity with increasing photon energies.

EXPERIMENTAL RESULTS

Figure 1 shows the Raman spectra of both samples *B* and *A* for laser-light incident on one of the cleavage faces and polarized parallel to the long axis of the crystal. No polarizer was used to analyze the scattered radiation. The two spectra are essentially identical, except for the larger background at low frequencies in sample *A* due to photoluminescence. Both samples show three well-defined peaks at 290, 338, and 624 cm^{-1}. The peaks at 290 and 338 cm^{-1} are narrower with a FWHM of 16 and 20 cm^{-1}, respectively, while the 625 cm^{-1} peak is noticeably wider with a FWHM of 32 cm^{-1}. These linewidths include a spectrometer resolution of about 5 cm^{-1}.

We have studied polarized Raman scattering from sample *B* where the laser is incident on two of the adjoining cleavage surfaces. We will denote these two surfaces as surfaces *A* and *A'*. Since we have no way of determining which of these two surfaces is oriented along the [110] or [1$\bar{1}$0] direction, we have arbitrarily assigned the *A* surface the [110] direction and the *A'* surface the [1$\bar{1}$0] direction. We will use the notation (X,Y) to specify the scattering configuration. In this notation X and Y are respectively the polarizations of the incident and scattered light. According to the Raman tensors shown earlier, the B_g mode should be forbidden in the configuration (Z',Z'). We found that indeed both the 338- and 624-cm^{-1} peaks disappeared in this configuration, consistent with the Raman tensor of the B_g mode. In sample *A* we also found that there is one polarization where both the 338- and 624-cm^{-1} peaks disappeared. Thus, our identification of the symmetry of the 338- and 624-cm^{-1} peaks agrees with that proposed by Chrzanowski and Irwin.[4] The intensity of the 290-cm^{-1} peak, although not zero, turns out to be weakest for the (Z',Z') configuration also.

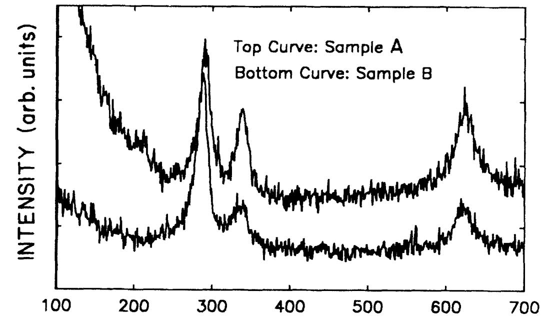

FIG. 1. Room-temperature Raman spectra of two single crystals of CuO grown in two different laboratories using two different techniques.

We also found that the 290-cm^{-1} peak was strongly polarized along an axis (which will be referred to as α) inclined at an angle to the long axis of sample *B*. This effect was observed for both surfaces *A* and *A'*. Figure 2(a) shows the dependence of the intensity of the 290-cm^{-1} peak on the angle between the polarization of the incident laser and the long axis of the crystal when the laser was incident along the *A'* surface. No analyzer was used in this measurement. The solid circles in Fig. 2(a) are data points. It is clear that the Raman intensity is strongest along an axis inclined about 120° to the axis of the crystal. By fitting the data points to the expression

$$I_s = I_0 \cos^2(\theta - \theta_0) , \qquad (1)$$

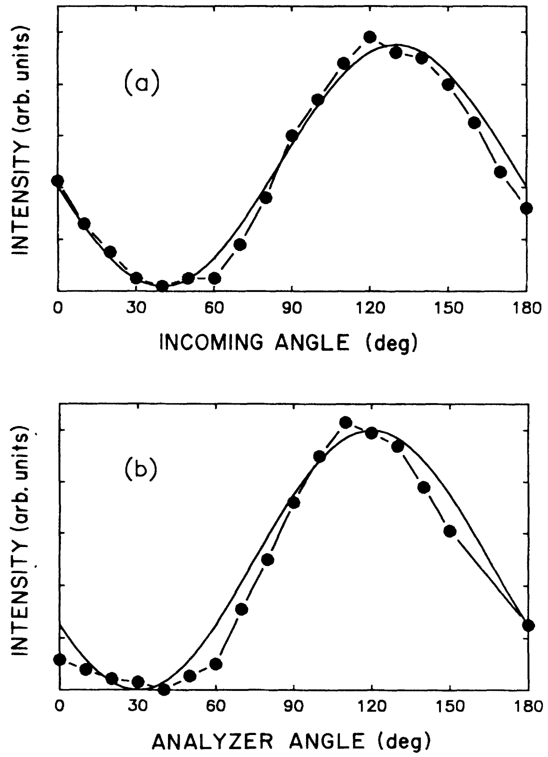

FIG. 2. (a) Raman intensity of the 290-cm^{-1} mode of CuO as a function of the angle between the incident laser polarization relative to the axis of Sample *B*. No analyzer was used in this case. (b) Raman intensity of the 290-cm^{-1} mode as a function of the angle between the analyzer and the axis of Sample *B*. The incident laser was polarized along the *Y'* axis in this case. In both cases the sample surface is *A'*.

we found that the angle between α and the axis of the crystal is 127 ± 5°. Not only is the Raman intensity of the 290-cm^{-1} mode strongest along α, it is almost completely polarized along α. When the laser was incident on the A' surface and polarized along the Y' axis, an analyzer was placed between the sample and the spectrometer. The intensity of the 290-cm^{-1} peak was measured as a function of the analyzer angle relative to the axis of the crystal. The results are shown in Fig. 2(b). When the data points are fitted with Eq. (1) the value of θ_0 determined is 120 ± 5°, showing that, within the experimental uncertainty, the scattered radiation is also polarized along α. Similar results were obtained when the experiment was repeated on the A surface except the orientation of α relative to the long crystal axis was found to be 70 ± 5°. From these results we concluded that α is not contained in either A or A' but is approximately inclined at equal angle to both surfaces while its projection onto surface A' is inclined at about 120° to the crystal axis.

The 625-cm^{-1} mode show a somewhat different polarization dependence than the 290-cm^{-1} mode. When the laser is incident on the A' surface, the dependence of its scattering intensity on the polarization of the incident radiation relative to the axis of the crystal sample are better fitted by the expression

$$I_s = I_0 \cos^2(\theta - \theta_0) + C . \tag{2}$$

The value of θ_0 for the 625-cm^{-1} mode was found to be 115 ± 5°. When the polarization of the incident laser was then set at 120° to the crystal axis and the intensity of the 624-cm^{-1} peak determined as a function of the analyzer angle, the value of θ_0 deduced by fitting the data points with Eq. (2) was 114 ± 5°. This shows that the intensity of the 624-cm^{-1} mode is also partially polarized along α.

DISCUSSION

Raman scattering in CuO powder has been reported by Rosen *et al.*[3] and Chrzanowski and Irwin.[4] Rosen *et al.*[3] found three peaks at 300, 346, and 630 cm^{-1}. Chrzanowski and Irwin[4] prepared their sample by compressing and sintering CuO powder into pellets. They found a total of five Raman peaks with frequencies: 218, 303, 350, 465, and 636 cm^{-1}. From group theoretical analysis, Chrzanowski and Irwin expected only three Raman-active optical phonons in CuO: two B_g modes and one A_g mode. They identified tentatively the 350- and 636-cm^{-1} peaks with the B_g modes and the 303-cm^{-1} peak as the A_g mode. From the temperature dependence of the 218-cm^{-1} mode, they suggested that it might be associated with one magnon scattering arising from the antiferromagnetic ordering of the Cu^{2+} ions.

As shown in Fig. 1, we have been able to identify only three peaks in Raman spectra obtained from our two CuO samples grown by two entirely different techniques. Except for the larger background in sample A, due presumably to impurities, the Raman spectra of the two samples are essentially matched within experimental uncertainties. The signal-to-noise ratios and linewidths of peaks in our spectra are all comparable to those reported by Chrzanowski and Irwin.[4] In both CuO samples, we did not observe any features around 218 and 465 cm^{-1}. Due to the quite different history of the samples involved, we do not have any explanation for the absence of these two peaks in our spectra. We can, however, conclude that the three peaks at 290, 338, and 624 cm^{-1} are most likely associated with optical-phonon modes of CuO, since they are observed by all three groups. Furthermore, from polarized Raman spectra we found that the symmetries of these modes are consistent with those proposed by Chrzanowski and Irwin.

Our result that the 290-cm^{-1} mode in CuO is strongly polarized along a particular axis which we have labeled α is not predicted by the Raman tensor. This result suggests that either certain components of its Raman tensor vanish, or that there are cancellations between different components of the Raman tensor. By noting that the crystal axis $(11\bar{2})$ is inclined at an angle of 116.3° to the crystal axis when projected onto the A surface, we suggested that α is probably related to the $(11\bar{2})$ axis.

CONCLUSIONS

By studying polarized Raman scattering in a single crystal of CuO grown by two different techniques, we have identified the symmetry of the three Raman-active optical phonons in CuO. We found that the 290-cm^{-1} mode is strongly polarized along one axis inside the crystal. This suggests that there are cancellations among the Raman tensor components of this mode when projected along this axis. Without further lattice-dynamic calculations we cannot explain why this cancellation occurs for this Raman mode in CuO.

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