

Evidence for a strong spin-phonon interaction in cupric oxide

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When CuO is cooled below its Néel temperature ($T_{N2}=213$ K) the onset of long-range magnetic order effectively increases the unit-cell dimensions and additional peaks, corresponding to zone-folded phonons, appear in the Raman spectrum. The zone-folding mechanism in CuO is unusual in that one of the folded phonons hardens significantly in frequency as the sample is further cooled below T_{N2} . It is shown that this dependence on temperature is determined by the sublattice magnetization and that the unusually large shift in frequency is caused by a strong spin-phonon interaction in cupric oxide.

The discovery¹ of high-temperature superconductivity generated renewed interest in cupric oxide (CuO), which has chemical and magnetic properties that are in many respects similar to those of the undoped high- T_c cuprates. For example CuO undergoes² a transition to an antiferromagnetically ordered state that is characterized by a relatively high Néel temperature and by a superexchange coupling constant³ $J\sim 80$ meV that is comparable to the values^{4,5} found in the undoped cuprates. Given these similarities it was anticipated that cupric oxide could serve as a relatively simple reference system in which one could probe the copper-oxygen interactions that are generally assumed to be fundamental to the occurrence of superconductivity in the high- T_c cuprates. The magnetic interactions of the Cu-O system are of particular interest given the possibility⁶ that antiferromagnetic (AFM) spin fluctuations could induce pairing in the high- T_c superconductors.

Several neutron-scattering,⁷⁻⁹ Raman-scattering,¹⁰⁻¹⁴ and far infrared (FIR)¹⁵⁻¹⁷ experiments have been carried out to investigate the lattice dynamics and antiferromagnetic ordering in CuO. It has been established^{7,8} that cupric oxide undergoes a transition at $T_{N2}=213$ K to a commensurately ordered AFM state. In Raman spectra obtained prior to this work the most obvious aspect that appeared to be related to AFM ordering in CuO is the appearance,^{10,11,13} for temperatures below 213 K, of a weak feature at about 230 cm^{-1} . As the temperature is further lowered this feature grows in intensity, becomes sharper and hardens in frequency to about 240 cm^{-1} for $T\leq 60$ K. The origin of this peak represents something of a puzzle in that neutron-scattering experiments⁷⁻⁹ do not provide any evidence of a structural transition and a possible assignment to one-magnon scattering was also incompatible with neutron results.³ Interpretations¹¹ in terms of scattering from a magnetic excitation yielded poor agreement with experiment. It was also anticipated^{12,15} that magnetic ordering and phonon modulation of the exchange constant might lead¹⁸⁻²⁰ to zone folding and hence to the appearance of new features at low temperatures. In previous reports¹⁹⁻²² however, as for other types²³ of structurally induced zone folding, the frequencies of the folded modes remain approximately constant and their inten-

sities increase very abruptly, when T is reduced below the transition temperature, in sharp contrast to the behavior observed for the 240 cm^{-1} mode. Although the zone-folding scenario in CuO seemed somewhat unlikely, experiments¹² were carried out on oxygen isotope exchanged samples, and the results implied a nonvibrational origin for the 240 cm^{-1} peak. Furthermore, recent FIR experiments¹⁷ on high-quality single crystals and isotope exchanged pressed pellets failed to reproduce earlier results¹⁵ that were suggestive of zone folding in CuO.

In an attempt to resolve this situation Raman experiments have been carried out on ⁶³CuO and ⁶⁵CuO samples. It has been found that the 240 cm^{-1} peak exhibits a Cu-isotope induced shift of $4.0\pm 0.5\text{ cm}^{-1}$ which, given the absence¹² of an O-isotope shift, implies a vibrational mode involving the motion of Cu atoms only. This result motivated us to carry out further experiments on high-quality single crystals with enhanced sensitivity. In the spectra obtained from these experiments four new features, in addition to the 240 cm^{-1} mode, are observed to appear when $T\leq T_{N2}$. The frequencies of all five of these features are in good agreement with phonon energies at the Z' zone-boundary point which have been measured⁹ using neutron-scattering techniques. These results thus demonstrate that the 240-cm^{-1} peak is vibrational in origin and its appearance in the spectra is due to a zone-folding mechanism. It will also be shown that a simple model, which incorporates a coupling between the phonons and the sublattice magnetization can be developed to explain the unusual temperature dependence that is observed for the frequency of the 240-cm^{-1} mode of CuO for $T\leq T_{N2}$. Finally it will be argued that the results of this paper demonstrate that there exists a strong spin-phonon interaction in CuO.

The Raman spectra presented in this paper were obtained with either the 514.5- or 488.0-nm lines of an argon-ion laser in a quasibackscattering configuration using the system described previously.^{11,12} Spectra have been obtained both from single crystals which were grown using a flux technique as described previously¹¹ and from pressed pellets of ⁶³CuO and ⁶⁵CuO. High-purity powders of ⁶³CuO (99.99%) and

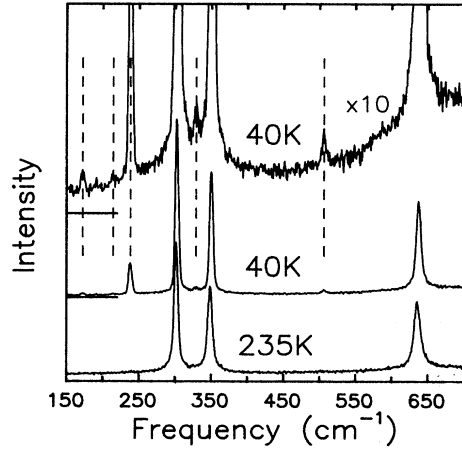


FIG. 1. Raman spectra obtained from a CuO single crystal at 235 K, a temperature well above the Néel temperature, and at 40 K which is well below the Néel temperature. The vertical dashed lines denote the positions of the new modes that appear in the spectrum when the sample is cooled below the Néel temperature.

^{65}CuO (99.5%) were pressed into disks about 0.7 cm in diameter and about 0.3 cm in thickness and sintered at 950 °C for 20 h. It should be noted that the two pellets were prepared using identical conditions.

CuO crystallizes²⁴ in a monoclinic structure (C_{2h}^6) with two (four) molecular units in the primitive (conventional) cell. Of the nine zone-center optical phonons three ($A_g + 2B_g$) are predicted¹¹ to be Raman active and at room temperature they occur at 303 (A_g), 350 (B_g), and 636 (B_g) cm^{-1} . These phonons are clearly visible in the spectra shown in Fig. 1 which were obtained from a good-quality single crystal. At $T_{N1} = 230$ K, CuO undergoes a transition to an incommensurately ordered AFM state and as the temperature is further lowered the samples undergo a further transition at $T_{N2} = 213$ K to a commensurately ordered AFM structure. In this work, we will focus on the low-temperature ($T \leq 213$ K) commensurate phase which is characterized^{7,8} by AFM ordering with a propagation vector $\mathbf{q}_0 = (\mathbf{a}^* - \mathbf{c}^*)/2$ and by a sublattice magnetization that is aligned parallel to the b axis. The coupling mechanism in CuO is super exchange along the (1,0,-1) direction via an intervening oxygen ion where the Cu-O-Cu bond angles are about 146°.²⁴

Based on the magnetic structure^{7,8} of CuO one can define a primitive magnetic cell characterized by the vectors $\mathbf{a}_M = 2\mathbf{a}_0$, $\mathbf{c}_M = \mathbf{c}_0 - \mathbf{a}_0$, and \mathbf{b}_0 where $(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$ refer to the conventional crystallographic unit cell. Figure 2(a) represents a projection onto the (010) plane with Cu atom positions denoted by open circles for Cu(1) sites⁷ and double circles for Cu(2) sites and that up and down spins are denoted by + and -. The Brillouin zones corresponding to both the conventional and magnetic units cells are shown in Fig. 2(b) and from this figure it is clear that the Z' point of the crystallographic zone is folded into the center of the smaller magnetic zone. In this case Guntherodt *et al.*^{19,20} have shown that phonons at Z' will appear in the Raman spectra if their vibrational pattern results in a modulation of the exchange constant. From an analysis similar to that car-

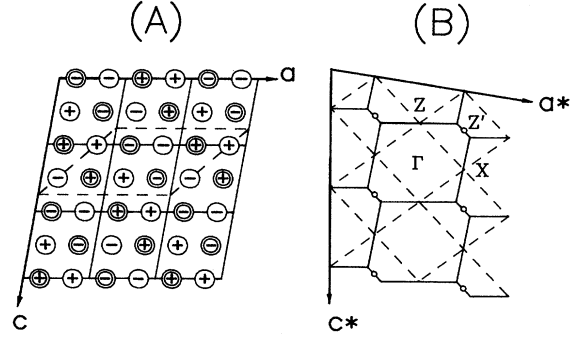


FIG. 2. (a) The projection of the magnetically ordered structure (Refs. 7 and 8) on the a - c plane where the dashed lines indicate the boundaries of a primitive cell (see text). The oxygen atoms are not shown. (b) The Brillouin zones corresponding to the crystallographic unit cell (Ref. 24) (solid lines) and the magnetic (Ref. 7) cell (dashed lines).

ried out in Ref. 20 it can be shown²⁵ that both the LA and TA modes at Z' , which are dominated by Cu-atom motion, will modulate J . The LA mode, which has eigenvectors along the chain, will be the most effective in this regard but the TA vibrations will also produce small variations in the Cu-O bond length and (perhaps more importantly) Cu-O-Cu bond angle. Optic modes involving longitudinal O-atom vibrations only (for example, the counterpart of the LA mode) should have very little effect on J but most of the optic modes will involve transverse vibrations of both the O or Cu atoms and will thus lead to a relatively small modulation of J . From these considerations we would expect the LA mode from Z' to have a strong presence in the spectra and several other phonons from the same zone-boundary point should appear as weaker features.

Raman spectra obtained from a single crystal both above and below the Néel temperature are shown in Fig. 1. As is evident from the figure, the low-temperature spectrum contains five additional modes at 175, 218, 240, 331, and 508 cm^{-1} . As mentioned above the 240 cm^{-1} mode shows a significant variation in both intensity¹¹ and frequency (see Fig. 4). In contrast to the 240- cm^{-1} peak the intensities and frequencies of the other four features remain approximately constant for all $T \leq 200$ K. The frequencies of the five new features are in good agreement (see Table I) with phonon frequencies at the Z' zone-boundary point (at \mathbf{q}_0) that have been measured⁹ by neutron scattering. It is thus suggested that these five features correspond to phonons from the Z' zone-boundary point at \mathbf{q}_0 and furthermore that the 240 cm^{-1} mode is the longitudinal-acoustic phonon at Z' .

TABLE I. A comparison of the phonon frequencies at Z' as measured by neutron scattering (Ref. 9) with the frequencies of the five new features that appear in the Raman spectra of CuO when $T \leq 210$ K.

Neutron (THz)	5.3	6.7	7.3	9.9	12.9	15.4	18.9
(cm^{-1})	177	223	243	330	430	513	630
Raman (cm^{-1})	175	218	240	331		508	??

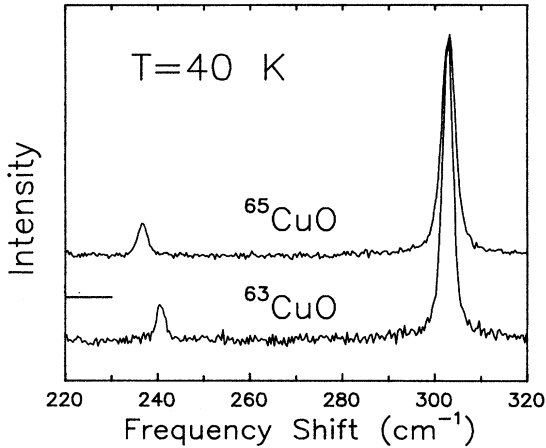


FIG. 3. The Raman spectra obtained at 40 K from a pressed and sintered pellet of ^{65}CuO (top curve) and ^{63}CuO (bottom curve) clearly indicating the 4 cm^{-1} shift induced by the exchange of copper isotope.

This assignment is consistent with the Raman spectra obtained at 40 K from pressed and sintered pellets of ^{63}CuO and ^{65}CuO which are shown in Fig. 3. A careful examination of these spectra reveals first that all three Raman active phonons (at 303 , 350 , and 636 cm^{-1}) have the same frequency in the two spectra. This observation is in agreement with expectations,¹¹ since these modes involve motion of the O atoms only and hence should be unaffected by Cu isotope exchange. The 240 cm^{-1} feature of ^{63}CuO however, shifts to 236 cm^{-1} in spectra (Fig. 3) obtained from the ^{65}CuO sample. If we consider a simple diatomic chain as representing the crystal in the $(1, 0, -1)$ direction then the acoustic-mode frequency at the zone boundary should be, since Cu is the heavier of the two atoms, given approximately by $\omega = (2K/M_{\text{Cu}})^{1/2}$. Based on this simple picture the absence of an oxygen-isotope shift and the observation of a Cu-isotope shift are thus completely consistent with a zone-boundary LA phonon assignment for the 240 cm^{-1} mode.

On folding, the zone-boundary LA mode becomes a zone-center mode breathing along $(1, 0, -1)$ directions. Such a mode should be Raman allowed in the xx , yy , zz , and xz scattering geometries, a prediction that is in accord with our observations. In addition, the temperature dependence¹¹ of the intensity is in good accord with the predictions of Ref. 18 (for $R=0$) for folding induced by exchange modulation. Finally, however, if the 240 cm^{-1} mode of CuO is to be interpreted as a zone-folded mode, one must account for the unusual temperature dependence of the frequency. As shown previously,¹¹ and in Fig. 4, the 240 cm^{-1} mode hardens significantly from about 228 cm^{-1} at 210 K to 240 cm^{-1} at 40 K and its intensity increases continuously until saturation at about 60 K . In previous observations in VI_2 (Refs. 19 and 20) and other compounds,²⁰ the intensity of the zone-folded modes rises quite abruptly just below the Néel temperature and their frequencies remain approximately constant as the sample is further cooled below T_N . The following analysis suggests that the anomalous temperature dependence of the 240 cm^{-1} phonon results from a strong interaction of this phonon with the magnetization in CuO. To model this inter-

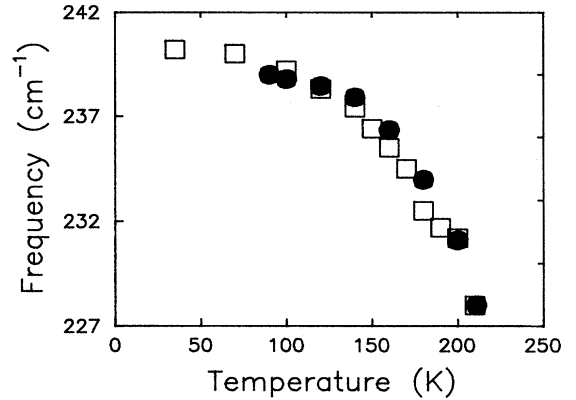


FIG. 4. A comparison of the measured Raman frequencies (open squares) of the 240-cm^{-1} mode with the model prediction (solid circles) as described in the text. The open squares represent an average of points measured in the present work and the results of previous measurements (Ref. 11) on a different single crystal.

action, we again consider a simple diatomic chain. The displacements of the Cu atoms from their equilibrium positions in association with the LA zone-boundary mode can be described by

$$\mathbf{u}(\mathbf{r}) = u_0 \hat{\mathbf{r}} \exp(i\mathbf{q}_0 \cdot \mathbf{r}), \quad (1)$$

where $\hat{\mathbf{r}} = \sqrt{2}/2(1, 0, -1)$.

Using the Ising model, the potential energy arising from the spin interactions can be written as

$$V_s = -\frac{1}{2} \sum_{ll'} J(\mathbf{r}_{ll'}) \mathbf{S}_y(\mathbf{r}_l) \cdot \mathbf{S}_y(\mathbf{r}_{l'}), \quad (2)$$

where $J(\mathbf{r}_{ll'})$ represents the super-exchange interaction between the spins of the l th and l' th copper ions, and $\mathbf{r}_{ll'}$ is the interspin distance. For simplicity we consider only nearest-neighbor interactions and expand $J(\mathbf{r}_{ll'})$ about the equilibrium interspin distance \mathbf{r}_0 up to the second order in the displacements:

$$J(\mathbf{r}_{ll'}) = J_0(\mathbf{r}_0) + A(\mathbf{r}_{ll'} - \mathbf{r}_0) + B(\mathbf{r}_{ll'} - \mathbf{r}_0)^2. \quad (3)$$

Substituting (1) and (3) into (2) yields (the sum over the linear term vanishes):

$$V_s = N(J_0 S^2 + 4B u^2 S^2), \quad (4)$$

where $S^2 = [S(T)]^2 = -\langle \mathbf{S}_y(\mathbf{r}_i) \cdot \mathbf{S}_y(\mathbf{r}_{i+1}) \rangle$ is the average value of the magnetization squared over all lattice sites and N is the total number of Cu sites in the chain. Then in the harmonic approximation the total potential energy can be written as

$$V = V_0 + NKu^2/2 + NJ_0 S^2 + 4NBu^2 S^2, \quad (5)$$

where V_0 is the part of potential energy that is independent of u and S . The last term in (5) represents the spin-lattice interaction and leads directly to an effective increase of the spring constant K . The frequency ω is now given by

$$\omega(T) = (\omega_0^2 + 4B' S^2)^{1/2} \quad (6)$$

where $\omega_0 = (2K/M_{\text{Cu}})^{1/2}$ is the bare frequency in the absence of spin-lattice interaction and $B' = B/M_{\text{Cu}}$. The growth of the sublattice magnetization $S(T)$ with decreasing temperature gives rise to the temperature dependence of the phonon frequency. Figure 4 is a comparison of the measured temperature dependence of the frequency shift of the 240-cm⁻¹ mode (open squares) with the prediction (filled circles) of Eq. (6) where $S^2(T)$ is taken from a neutron-scattering result by Yang *et al.*⁸ $\omega_0 = 228$ cm⁻¹ and B' is treated as a constant and used as a fitting parameter. As is evident from the figure there is an excellent agreement between the two sets of points.

For comparison purposes Eq. (6) can be expanded as $\omega(T) \approx \omega_0 + \lambda(\mathbf{S}_i \cdot \mathbf{S}_{i+1}) = \omega_0 - \lambda S^2(T)$. Assuming $S^2(40 \text{ K}) \approx S^2(0) \approx \frac{1}{4}$ (for the Cu-O chain), the spin-phonon coupling coefficient $\lambda = -2B'/\omega_0$ is estimated to be about -50 cm⁻¹, which indicates that the spin-phonon interaction in CuO is much stronger than previously studied²¹ antiferromagnetic materials such as FeF₂ and MnF₂, where $|\lambda| \leq 1.0$ cm⁻¹.

The behavior of the remaining zone-folded modes at 175, 218, 331, and 508 cm⁻¹, is more conventional in that their intensities and frequencies remain approximately constant as T is reduced below T_c . This behavior is consistent with our previous discussion in that the LA phonon at $Z'(240)$ should strongly modulate J while the vibrational patterns of the TA (175, 218) and optic modes (331 and 508) should provide a

relatively weak modulation of J . The absence of the 430-cm⁻¹ mode in the Raman spectra could suggest that it arises from longitudinal vibrations of the O atoms (the linear chain counterpart of the 240 mode). Finally the mode occurring at 630 cm⁻¹ in the neutron spectra would be masked in the Raman spectra by the strong Bg phonon.

In conclusion five new modes appear in the Raman spectrum of CuO when it is cooled below $T_{N2} = 213$ K. From measurements on samples grown with different Cu isotopes and comparisons with neutron measurements it is concluded that these modes correspond to phonons that are zone folded from the Z' point of the Brillouin-zone boundary. A zone-folded mode at 240 cm⁻¹ exhibits an unusually large variation in intensity and frequency with decreasing temperature for $T \leq T_{N2}$. It has been shown that this temperature dependence occurs because of the presence of a very strong interaction of the phonon with the magnetization in cupric oxide. This type of interaction, and the zone-folding mechanism observed here, could also be present in the undoped high- T_c cuprates and furthermore could play a role in determining some of their very interesting superconducting²⁶ and optical²⁷ properties.

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