Pressure dependence of the nuclear resonance of antiferromagnetic CuO

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(Received 9 May 1991)

The pressure dependence of the ^{63}Cu NMR of a single crystal of CuO has been measured in the antiferromagnetic state at 77 K. The magnitude of the effective magnetic field at the nucleus (ν_L, the Larmor frequency) was found to decrease with pressure, $\partial \ln \nu_L / \partial P = -1.39$ Mbar^{-1}. The electric-field gradient ($q_{zz}^{\rm tot}$) at the nucleus increases such that $\partial \ln q_{zz}^{\rm tot} / \partial P = 5.3$ Mbar^{-1}, while the value calculated for external point charges is -2.7 Mbar^{-1}. The observed value of $\partial \ln q_{zz}^{\rm tot} / \partial P$ must therefore arise from a redistribution of electrons over the copper $3p$ and $3d$ orbitals.

There have been a large number of experimental and theoretical investigations of the electric field gradient (EFG) at the copper nuclei of high-T_c superconductors such as $YBa_2Cu_3O_7$ and of related insulating oxides, because the EFG is sensitive to the nature of the copper—oxygen bond. The magnitude of the EFG may be measured using NMR or NQR (nuclear quadruple resonance). Recent NQR experiments[1] on Cu_2O and CuO at room temperature have shown that additional information on the copper—oxygen bond may be obtained by measuring the NQR frequency (ν_Q) as a function of hydrostatic pressure. In the case of Cu_2O, for example, it has frequently been assumed that the bonding is purely ionic and therefore that copper is a monovalent ion with a full $3d$ shell. The value of $\partial \ln \nu_Q / \partial \ln V$ for such an ionic compound would be -1 but in fact the value for Cu_2O was found to be -1.5, showing that the copper—oxygen bond has some covalent character.

The EFG at the Cu(2) site of $YBa_2Cu_3O_7$ is of particular interest at present because calculations[2,3] suggest that it is extremely sensitive to the distribution of electrons over the $3d$ and/or $3p$ orbitals. While there have been many NQR experiments performed on $YBa_3Cu_3O_7$ at atmospheric pressure, the value of $\partial \ln \nu_Q / \partial P$ at the Cu(2) site is only known[4] to an accuracy of $\sim 50\%$ because of the technical difficulties associated with the accurate measurement of a small change in the frequency of a broad NQR line. We have therefore studied CuO since (a) the dominant (planar) copper-oxygen interaction is similar to that at the Cu(2) site of $YBa_2Cu_3O_7$ and (b) Shimizu *et al.* have shown[5] that the values of ν_Q for CuO and the Cu(2) site of $YBa_2Cu_3O_{7-\delta}$ satisfy the same linear function of the ionic EFG in the crystals. We find that the EFG at the ^{63}Cu nucleus in CuO is extremely sensitive to pressure, supporting the theoretical picture of the EFG at the Cu(2) site, but that the value of $\partial \ln \nu_Q / \partial P$ does not change between the paramagnetic state at room temperature and the antiferromagnetic state at 77 K. It would therefore seem to be valid, as has previously been assumed,[6] to neglect magnetic interactions in the calculation of the EFG of, e.g., $YBa_2Cu_3O_6$.

The zero field NMR of ^{63}Cu in a single crystal of CuO at 77 K was measured using a phase coherent swept frequency spectrometer.[7] The sample was placed in a coil inside a liquid-filled pressure lock cell. The cell was pressurized at room temperature and could then be cooled to 77 K in liquid nitrogen. The pressure was measured using a semiconductor pressure transducer.

In the present experiment the single crystal provided no more information than a powder but the ^{63}Cu linewidth of the single crystal of CuO at 77 K (0.5 MHz) was narrower than that found[8] in powder samples (2 MHz) allowing a more accurate value to be found for the pressure dependence of the NMR lines. The ^{63}Cu line shapes were obtained from the integral of the spin echo signal as function of frequency. At 77 K the NMR spectrum consists of three lines, Fig. 1. The central line is largely due to the magnetic interaction of the ^{63}Cu nuclear moment with the ordered electronic moments on the copper ions in the antiferromagnetic state, and the two satellite lines are due to the quadrupole interaction with the EFG. The pressure dependence of the lines is shown in Fig. 2 and the results summarized in Table I.

The three-line spectrum shown in Fig. 1 for CuO at atmospheric pressure was fitted to an accuracy of ± 0.01 MHz by the parameters characterizing the Larmor frequency (ν_L) and the electric quadrupole frequency (ν_Q) shown in Table I with $\theta = 9°$, $\phi = 0°$, and $\eta = 0.20$, in agreement with earlier work[8] at 4.2 K. Here θ, ϕ are the polar angles of the local magnetic field with respect to the principal axes of the EFG and $\eta = (q_{xx}^{\rm tot} - q_{yy}^{\rm tot})/q_{zz}^{\rm tot}$ in a set of principal axes such that $|q_{zz}^{\rm tot}| > |q_{yy}^{\rm tot}| > |q_{xx}^{\rm tot}|$. The experimental value of η is reasonably close to the value (0.3) calculated assuming a lattice of Cu^{2+} and O^{2-} ions. The pressure dependence of the three ^{63}Cu NMR lines was similarly analyzed to isolate the contributions of the magnetic field and electric field gradient.

The structure of CuO is monoclinic (space group

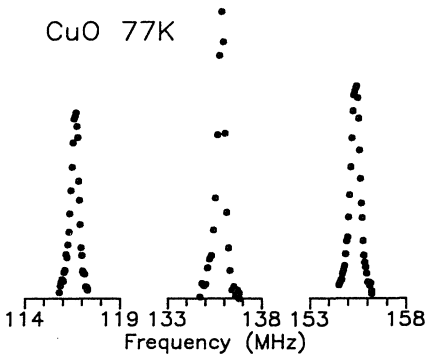

FIG. 1. The zero field ^{63}Cu NMR of antiferromagnetic CuO at 77 K and atmospheric pressure.

$C2/c$) with lattice constants at room temperature $a=4.6837$, $b=3.4226$, $c=5.1288$ Å, $\beta=99.54°$, where β is the angle between a and c. The unit cell contains four copper atoms at the 4c positions $(\frac{1}{4},\frac{1}{4},0)$, etc., and four oxygen atoms at the 4e positions $(0,y,\frac{1}{4})$, etc. Although between 295 K and 77 K CuO undergoes two magnetic transitions,[9] to incommensurate antiferromagnetism at 230 K and commensurate antiferromagnetism at 213 K, the change in the value of ν_Q shown in Table I may be largely due to thermal expansion rather than any influence of magnetic order on the EFG. The linear thermal expansion (α) and compressibility (δ) of CuO are extremely anisotropic[10] but (α/δ) for each crystal axis is roughly constant. The a (c) axis of CuO expands (contracts) with increasing temperature or pressure so that the planar oxygen contribution to the EFG remains nearly constant.

The value[10] of $\partial \ln b/\partial T$ near 295 K is -19×10^{-6} K^{-1} and of $\partial \ln b/\partial P$ -0.92 Mbar^{-1}, i.e., a temperature change of 1 K produces the same change of length as a presure of 21 bar. The value of $\partial \ln \nu_Q/\partial P$ at 295 K is 5.4 Mbar^{-1} so the application of a pressure of 21 bar leads to a frequency shift of 2.3 kHz which may be compared to the experimental value[11] for $\partial \nu_Q/\partial T$ of 2.4 kHz K^{-1} in the temperature range 200–500 K. Near room temperature therefore, ν_Q is only a function of the volume of the

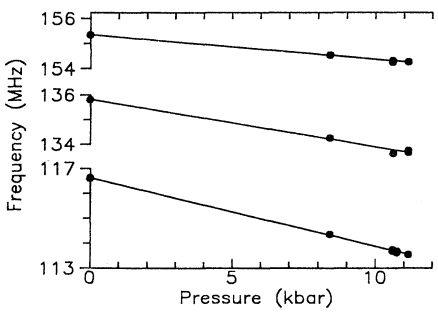

FIG. 2. Pressure dependence of the zero field ^{63}Cu NMR of CuO at 77 K.

TABLE I. NMR frequencies of ^{63}Cu in CuO at 77 K and the derived values of the magnitude of the magnetic (ν_L) and electric (ν_Q) interaction. The value of ν_Q at 295 K is also shown.

T (K)	ν ($P=1$ at) (MHz)	$(\partial \ln \nu/\partial P)$ (Mbar^{-1})
77	155.35	−0.63
77	135.82	−1.42
77	116.64	−2.37
77	$\nu_L=135.89$	−1.39±0.07
77	$\nu_Q=20.03$	5.3±0.2
295	$\nu_Q=20.64$	5.4±0.1

unit cell of CuO. The change in the value of ν_Q from 20.03 MHz at 77 K to 20.64 MHz at 295 K may therefore be due purely to thermal expansion, but more detailed measurements of the lattice constants of CuO as a function of temperature are required before this can be established. The insensitivity of ν_Q to the AFM state of CuO is also shown by the fact that $\partial \ln \nu_Q/\partial P$ does not change within experimental error, between 295 K and 77 K.

The value of ν_Q for ^{63}Cu ($I=\frac{3}{2}$) is given by

$$\nu_Q = e^2 Q q_{zz}^{\text{tot}} (1+\eta^2/3)^{1/2}/2h \ , \tag{1}$$

where Q is the nuclear quadrupole moment (-0.211 b). The value of q^{tot} is usually considered to arise from the influence of external charges (q^{ionic}) and from a valence contribution if there are holes in the 3d shell, i.e., if the Cu ion is not in the state Cu^+. We define

$$\nu_Q = \nu^{\text{ionic}} + \nu^{\text{val}} \ , \tag{2}$$

$$\nu^{\text{ionic}} = (1-\gamma_\infty) e^2 Q q_{zz}^{\text{ionic}} (1+\eta^2/3)^{1/2}/2h \ , \tag{3}$$

and note that, while ν^{ionic} and ν^{val} may be of either sign, only the magnitude of ν_Q is given by NQR. In Eq. (3) q_{zz}^{ionic} is the EFG calculated using the assumed charges at each lattice site and $(1-\gamma_\infty)$ is the Sternheimer antishielding factor which allows for the influence of q^{ionic} on the electron shells around the Cu nucleus. A discussion of the values of γ_∞ for the different valence states of Cu has been given by Garcia and Bennemann.[12] The theoretical value of γ_∞ for Cu^{2+} is -7.6 but it is difficult to verify this value by experiment. The value of γ_∞ is not expected to be a function of pressure.

A lattice sum for CuO, assuming Cu^{2+} and O^{2-} ions, leads to $\nu^{\text{ionic}}/(1-\gamma_\infty)=-2.70$ MHz. In an analysis of the NQR of ^{63}Cu in CuO at room temperature,[1,12] ν_Q was taken to be positive and the value of γ_∞ was taken to be -7.6. The values of ν^{ionic} (ν^{val}) are then -23.2 (43.9) MHz. Shimizu *et al.* however, have shown[5] that for ^{63}Cu in CuO, and the Cu(2) site of both insulating and superconducting samples of $YBa_2Cu_3O_{7-\delta}$, the values of ν_Q are a linear function of q_{zz}^{ionic} with a value of $\gamma_\infty \sim -20$, i.e., ν^{ionic} (ν^{val}) equal to -56.7 (77.3) MHz for CuO. These empirical results are in sharp contrast to the conclusion of the LAPW calculations[2,3] that the contributions of ν^{ionic} to ν_Q is negligible for $YBa_2Cu_3O_{7-\delta}$.

The interpretation of the measured pressure depen-

dence of the EFG at the ^{63}Cu nucleus of CuO is complicated by the highly anisotropic compressibility of the material. In an elastically isotropic material, such as Cu_2O, any deviation of $(\partial \ln \nu_Q / \partial \ln V)$ from the value -1, i.e., $(\partial \ln \nu_Q / \partial \ln \nu_Q^{\text{ionic}}) = 1$, is an indication that the bonding is not purely ionic. This is not the case for CuO where[10] $\partial \ln(a,b,c)/\partial P = (+0.29, -0.92, -0.18)$ Mbar^{-1}. Using these values of the linear compressibility the value of $(\partial \ln \nu^{\text{ionic}}/\partial P)$ is -0.28 Mbar^{-1} and $(\partial \ln \nu^{\text{ionic}}/\partial \ln V) = 0.29$. However, it appears[13] that the oxygen y parameter of CuO is also a function of pressure, $(\partial \ln y / \partial P) = -0.79$ Mbar^{-1}, and including this variation in the calculation leads to $(\partial \ln \nu_Q^{\text{ionic}}/\partial P) = -2.7$ Mbar^{-1} or $(\partial \ln \nu_Q^{\text{ionic}}/\partial \ln V) = +2.8$. It is clear therefore that a knowledge of the oxygen y parameter is essential for the calculation of $(\partial \ln \nu_Q^{\text{ionic}}/\partial P)$.

The value of $(\partial \ln \nu^{\text{val}}/\partial P)$ for CuO may be calculated as a function of $(1-\gamma_\infty)$ from Eqs. (1) and (2), using the experimental value of $(\partial \ln \nu_Q / \partial P) = 5.3$ Mbar^{-1} and the value of -2.7 Mbar^{-1} for $(\partial \ln \nu_Q^{\text{ionic}}/\partial P)$ calculated above, and is 5.3, 1.0, -0.61 Mbar^{-1} for $(1-\gamma_\infty) = 0$, 8.6, 21, respectively. These values of $(1-\gamma_\infty)$ represent the cases where (a) the ionic contribution is negligible, (b) the theoretical value for Cu^{2+} is used, and (c) the empirical value for CuO and the Cu(2) site of $YBa_2Cu_3O_{7-\delta}$ given by Shimizu *et al.* is used. There are no first principles calculations of the EFG of CuO at present but it would be interesting to repeat the LAPW calculations for the Cu(2) site of $YBa_2Cu_3O_7$ at a reduced volume to find the value of $(\partial \ln \nu_Q / \partial P)$.

The magnitude of the effective field at the Cu^{63} nucleus of CuO at 77 K (120.4 kG) is in agreement with the value of 121.5 kG found[8] at 4.2 K in view of the Néel temperature of 230 K. Shimizu *et al.* have analyzed[5] the temperature dependence of the Knight shift of ^{63}Cu in paramagnetic CuO to give a hyperfine coupling constant ($A^{\parallel}$) of -146 ± 10 kOe/μ_B, i.e., the effective field is antiparallel to the moment of the parent copper ion. The ordered moment on each copper ion in the antiferromagnetic state at 0 K is $(0.68 \pm 0.1)\mu_B$ (Ref. 9) from which $A^{\parallel}_{AF} = -179 \pm 23$ kOe/μ_B. The reason for the decrease of the ^{63}Cu NMR frequency of CuO at 77 K under pressure is not obvious at present but we calculate that the Cu—O—Cu bond angle associated with the antiferromagnetic coupling increases from 145° at atmospheric pressure[9] by 0.2°/kbar. This would increase the contribution of the supertransferred hyperfine field and hence decrease the overall (negative) hyperfine field at the Cu nucleus.

CONCLUSION

It has been shown that the measurement of the ^{63}Cu NQR frequency (ν_Q) of CuO as a function of pressure provides valuable information on the bonding of CuO, since the value of $(\partial \ln \nu_Q / \partial P)$ is twice that predicted by a point charge model and of opposite sign.

ACKNOWLEDGMENTS

We are indebted to Professor J. B. Forsyth for details of the compressibility of CuO in advance of publication and to Professor G. A. Sawatsky for a helpful conversation.

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