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LETTER TO THE EDITOR

Pressure dependence of the electric field gradient at the ^{63}Cu nucleus of Cu_2O and CuO; implications for the analysis of NQR measurements on high T_c superconductors

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Abstract. The electric field gradient (EFG) at the ^{63}Cu nucleus of Cu_2O and CuO has been measured as a function of pressure using the nuclear quadrupole resonance frequency (ν_Q). The value of $(\partial \ln \nu_Q/\partial P)_T$ was 1.40 ± 0.02 (1.33 ± 0.05) $Mbar^{-1}$ for Cu_2O at 295 (77) K and 5.4 ± 0.1 $Mbar^{-1}$ for CuO at 295 K. The value of $(\partial \ln \nu_Q/\partial \ln V)$ for Cu_2O is -1.5, showing that Cu_2O is not a purely ionic compound, as is often assumed in the analysis of the EFG of high T_c superconductors. The magnitude of $(\partial \ln \nu_Q/\partial P)_T$ for ^{63}Cu in CuO suggests that meaningful measurements of the pressure dependence of ν_Q in the high T_c superconductors can be made at easily accessible pressures.

The importance of the nature of the copper–oxygen bonds in high T_c superconductors and related compounds has lead to renewed interest in the properties of Cu_2O and CuO. The analysis of the bonding of the Cu(1) site in $YBa_2Cu_3O_6$ for example frequently begins, e.g. Garcia and Bennemann (1989), by assuming that Cu_2O is a purely ionic compound containing Cu^+ i.e. a full 3d shell. The electric field gradient (EFG) at the Cu(1) nucleus is then estimated by simply scaling the experimental value in Cu_2O by the ratio of the lattice sums in the two compounds. Since this procedure leads to reasonable agreement with experiment it was then concluded by Garcia and Bennemann that Cu(1) in $YBa_2Cu_3O_6$ may be considered to be Cu^+. At the Cu(1) site in $YBa_2Cu_3O_7$ and the Cu(2) sites in $YBa_2Cu_3O_{7-\delta}$ it is found that the EFG do not scale with the Cu–O distances, because even a fraction of a hole in the 3d shell will make a large contribution to the total EFG, and hence information about the valence of Cu at these two sites may be obtained from the measured EFG. However, different versions of such a point charge analysis, Adrian (1988), Garcia and Bennemann (1989) are not always in agreement as to the charges on the Cu sites in $YBa_2Cu_3O_{7-\delta}$ and also differ from the results of the first-principles calculation of Nagel (1985) and Schwarz *et al* (1990). It is therefore worth investigating the bonding in Cu_2O and CuO in more detail.

In this letter we present measurements of the nuclear quadrupole resonance (NQR) of ^{63}Cu in Cu_2O and CuO at high pressure. The NQR frequency (ν_Q) is a measure of the magnitude of the EFG at the nucleus, see equations (1–3) below. In a simple ionic

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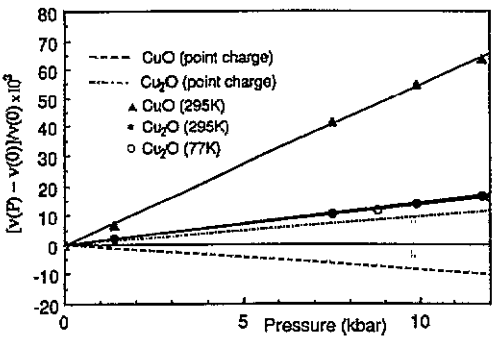

Figure 1. Pressure dependence of the ^{63}Cu NQR frequency in Cu_2O and CuO. Full lines represent linear least squares fits to the experimental data: broken lines show the predictions of a simple point charge model using compressibility data from table 1.

crystal $\partial \ln \nu_Q / \partial \ln V \sim -1$ while in a covalently bonded crystal containing no ions with unfilled shells, the value is ~0 e.g. Kushida *et al* (1956). The value of $\partial \ln \nu_Q / \partial \ln V$ for Cu_2O was found to be -1.5 and hence Cu_2O is not a purely ionic compound. The compressibility of CuO is only known for the *a* and *c* axes, table 1, but we estimate that $\partial \ln \nu_Q / \partial \ln V \sim -5$ and attribute this large value to a volume sensitive contribution to the EFG from the partially full Cu 3d shell.

The NQR of ^{63}Cu in Cu_2O and CuO was measured using a phase coherent swept frequency spectrometer, Dumelow and Riedi (1987). The samples of Cu_2O (powder) and CuO (single crystal) were placed in the same 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 NQR experiment the single crystal provided no more information than a powder but the ^{63}Cu linewidth of the single crystal of CuO (~100 kHz) was narrower than that found in powder samples, allowing a more accurate value to be found for $(\partial \ln \nu_Q / \partial P)_T$. The ^{63}Cu lineshape of CuO was obtained from the integral of the spin echo signal as a function of frequency. The ^{63}Cu linewidth in Cu_2O was sufficiently narrow (15 kHz at atmospheric pressure, 30 kHz at 10 kbar) for ν_Q to be obtained from the beats between the free induction decay and the reference oscillator. The pressure dependence of ν_Q for Cu_2O and CuO is shown in figure 1 and the results summarized in table 1.

In a non-cubic environment the NQR spectrum of ^{63}Cu ($I = 3/2$) is a single line at frequency ν_Q 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 (-0.211b), q_{zz}^{tot} the largest component of the total EFG in a set of principal axes such that $q_{zz}^{\text{tot}} > q_{xx}^{\text{tot}} > q_{yy}^{\text{tot}}$, and $\eta = (q_{xx} - q_{yy})/q_{zz}$. While first principles calculations of EFG are now being made, as will be discussed later, 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 equation (3) q_{zz}^{ionic} is the EFG calculated using the assumed charges at

Table 1. The pressure and temperature dependence of the lattice constants and ^{63}Cu NQR (ν_Q) of Cu_2O and CuO. See equations (1)–(3) for definitions of ν_Q and ν^{ionic}. The values of the Sternheimer anti-shielding factor (γ_∞) are discussed in the text. Note that only the magnitude of the EFG is obtained from experiment.

	T (K)	Cu_2O cubic	CuO monoclinic
$\partial \ln(a,b,c)/\partial T\,(10^{-6}\,K^{-1})$	195–295	≈0	$6 \pm 4^a, -19 \pm 3^a, -4 \pm 4^a$
$\partial \ln(a,b,c)/\partial P\,(Mbar^{-1})$	210	—	$0.47^b, -1.25^c, -0.20^b$
$(\partial P/\partial \ln V)_T$ (Mbar)	77	-1.10^d	—
	295	−1.06	—
ν_Q (MHz)	0	26.80	20.07^e
	77	26.70	—
	295	25.98	20.64
$(\partial \nu_Q/\partial T)_P$ (kHz K^{-1})	295	−3.5	2.2
$\partial \nu_Q/\partial P$ (Hz bar^{-1})	77	35.7 ± 1.5	—
	295	36.5 ± 0.5	111 ± 3
$\partial \ln \nu_Q/\partial P\,(Mbar^{-1})$	77	1.33 ± 0.05	
	295	1.40 ± 0.21	5.4 ± 0.1
$\partial \ln \nu_Q/\partial \ln V$	77	−1.46	—
	295	−1.48	—
$\nu^{ionic}/(1-\gamma_\infty)$ (MHz)	0	+4.01	−2.70

[a] See Forsyth *et al* (1988), table 1.
[b] Estimated, for pressures below 10 kbar, from data of Forsyth (1990).
[c] Scaled from the thermal expansion data.
[d] Hallberg and Hanson (1970).
[e] Antiferromagnetic state, Tsuda *et al* (1988).

each lattice site and $(1-\gamma_\infty)$ is the Sternheimer anti-shielding 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 (1989). The theoretical values of γ_∞ are $-17(Cu^+)$, $-7.6(Cu^{2+})$, $-7.1(Cu^{3+})$ but it is difficult to verify these values by experiment. The value of γ_∞ is not expected to be a function of pressure. Having chosen a value of γ_∞, the value of ν^{val} is derived from the experimental ν_Q using equation (2). It is clear from the discussion given by Adrian (1988), Garcia and Bennemann (1989) and Schwarz *et al* (1990) that the value of ν^{val} is large for any configuration except Cu^+ and is extremely sensitive to the relative occupation of the d orbitals.

The crystal structure of Cu_2O is cubic. The Cu ions form a FCC lattice so the Cu charges do not contribute to q^{ionic}. The EFG at the Cu site is dominated by a linear arrangement O—Cu—O. The lattice sum for O^{2-} leads to $\nu_Q^{ionic}/(1-\gamma_\infty) = +4.01$ MHz, and $\eta = 0$, while the low temperature limit of ν_Q is 26.8 MHz, table 1. The temperature dependence of ν_Q of Cu_2O at atmospheric pressure shown in table 1 may be understood as due to the thermal excitation of a transverse simple harmonic mode of the Cu^+ ion relative to the neighbouring O^{2-} with an Einstein temperature of 140 K, de Wijn and de Wildt (1966). While the thermal expansion of Cu_2O is not well known it is certainly small, of the order ppm K^{-1}, so the temperature dependence of ν_Q at atmospheric pressure is essentially that at constant volume.

Our value of $(\partial \ln \nu_Q/\partial P)_T$ for ^{63}Cu in Cu_2O at room temperature is in good agreement with an earlier measurement due to Kushida *et al* (1956). However, using the value

of the isothermal bulk modulus (B_T) given by Bridgeman (1932) for a powder compact of Cu_2O Kushida *et al* (1956) interpreted their measurements near room temperature as $\partial \ln \nu_Q/\partial \ln V = -1 + 7.6 \times 10^{-4}$ T i.e. an ionic term at 0 K plus a term due to the change, with pressure, of the force constant of the Einstein oscillator at the Cu site. This interpretation, which has been the basis for the common assumption that Cu_2O is an ionic compound, can no longer be sustained. The present value for $(\partial \ln \nu_Q/\partial P)_T$ for Cu_2O at 77 K is almost identical to that at 295 K, table 1, while the model of Kushida and co-workers predicts a difference of some 17%. Furthermore, it appears that the value of B_T for Cu_2O given by Bridgeman is in error by about a factor of two. The values of B_T shown in table 1, derived for ultrasonic experiments on a single crystal of Cu_2O by Hallberg and Hanson (1970), leads to $\partial \ln \nu_Q/\partial \ln V = -1.48$ (-1.46) at 295 (77) K which is quite different from the value of -1 for an ionic crystal.

The experimental value of $\partial \ln \nu_Q/\partial \ln V$ for Cu_2O may be understood qualitatively in terms of equations (1–3), since there must be an appreciable contribution to ν_Q from ν^{val} if Cu is not in the state Cu^+. The value of ν^{ionic} is $4(1 - \gamma_\infty)$ MHz and of $\nu^{valence}$ is $(22.8 + 4\gamma_\infty)$ MHz. Since γ_∞ presumably lies between the theoretical values of -17 for Cu^+ and -7.8 for Cu^{2+}, as discussed earlier, it is clear that ν^{ionic} is positive and $\nu^{valence}$ negative. Taking γ_∞ independent of pressure we find $\partial \nu^{val}/\partial P$ varies from ~ 0 for $\gamma_\infty = -8$, to -32 Hz bar^{-1} for $\gamma_\infty = -17$ i.e. *the valence contribution to* $\partial \nu_Q/\partial P$ *has the* opposite sign to $\partial \nu^{ionic}/\partial P$.

In fact, there is also strong theoretical support for the view that Cu_2O is not an ionic compound. Nagel (1985) used a cluster calculation to find the EFG in Cu_2O and concluded that the bonding was unusual, with no strong covalent bonds, but significant deviations from the simple ionic scheme of Cu^+ and O^{2-}. The cluster calculation gave a negative value of ν_Q but both the lattice sum and the linear augmented plane wave (LAPW) calculation of Blaha *et al* (1989) lead to a positive ν_Q. A repetition of the cluster and LAPW calculations at a different volume would enable their validity to be tested against our value of $(\partial \ln \nu_Q/\partial P)_T$.

The structure of CuO is monoclinic 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, see table 1 of Forsyth *et al* (1988). The most important contribution to the ionic EFG at the Cu site arises from four planar O^{2-} ions. Below 230 K CuO is an antiferromagnet of incommensurate structure with a transition to commensurate antiferromagnetism at 213 K, Forsyth *et al* (1988). The ordered magnetic state leads to a NMR spectrum in zero magnetic field of three broad lines centred on 137.1 MHz (Tsuda *et al* 1988) so we have only measured ν_Q for CuO near room temperature. The lattice constants of CuO are a weak function of temperature, see table 1 based on table 1 of Forsyth and co-workers, with only the value of $\partial \ln b/\partial T$ being much greater than experimental error. The value of $(\partial \ln \nu_Q/\partial T)_P$ near 295 K is small for CuO, table 1, so we expect that, as for Cu_2O, the value of $(\partial \ln \nu_Q/\partial P)_T$ will not be greatly influenced by a change in the vibrational spectrum of the ^{63}Cu nucleus with pressure.

A lattice sum over the CuO structure, assuming Cu^{2+} and O^{2-} ions, leads to $\nu^{ionic} = -23.6$ MHz, for ^{63}Cu, taking $\gamma_\infty = -7.6$ as described earlier and a value of $\eta = 0.3$ in fair agreement with the experimental value of 0.20, Tsuda *et al* (1988). While the magnitude of ν_Q^{ionic} is reasonably close to ν_Q, table 1, the valence contribution to the EFG cannot be neglected for Cu^{2+}. Following the reasoning of Garcia and Bennemann (1989) for Cu^{2+} in $YBa_2Cu_3O_{7-\delta}$ we calculate $\nu^{val} = \nu_Q - \nu^{ionic} = +44.2$ MHz i.e. ν^{ionic} and ν^{val} have the opposite sign as in $YBa_2Cu_3O_{7-\delta}$. This value of ν^{val} for CuO is only about

2 MHz different from that found for the Cu(2) sites in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ but we note that Adrian (1988) estimates that for Cu^{2+} in an ionic lattice, $\nu^{val} = 95.5$ MHz. In both CuO and $YBa_2Cu_3O_{7-\delta}$ therefore the number of holes in the Cu d shell must be less than one, indicating covalent bonding to the neighbouring oxygen.

The compressibility of CuO is highly anisotropic and has only been measured along the *a* and *c* axes at 230 K, table 1. In the absence of other data, we apply the same values to the present experiment at 295 K. The value of $(\partial \ln b/\partial P)_T$ for CuO has not been measured but must be negative, because $(\partial \ln V/\partial P)_T$ is always negative and, from table 1, the value of *ac* increases under pressure. Taking the compressibility of each lattice direction to be proportional to its thermal expansion leads to an estimate of $(\partial \ln b/\partial P)_T \approx -1.25\ \text{Mbar}^{-1}$ and $(\partial \nu^{ionic}/\partial P)_T \approx 20\ \text{Hz bar}^{-1} = 0.18(\partial \nu_Q/\partial P)_T$. The large positive value found for $(\partial \ln \nu_Q/\partial P)_T$, must therefore arise from the volume dependence of ν^{val} with $(\partial \ln \nu^{val}/\partial \ln P)_T \approx 2\ \text{Mbar}^{-1}$. The large pressure dependence of ν^{val} for CuO can be understood from the results of the LAPW calculations of Schwarz *et al* (1990), and the point charge calculations of Adrian (1988) and Garcia and Bennemann (1989), for $YBa_2Cu_3O_{7-\delta}$ which show that ν^{val} is extremely sensitive to the occupation of the 3d orbitals e.g. a transfer of 0.07 electrons from the $3d_{x^2-y^2}$ to the $3d_{z^2}$ orbital was found to increase the value of ν^{val} at the Cu(2) site in $YBa_2Cu_3O_7$ by a factor of two.

In conclusion, high pressure ^{63}Cu NQR measurements of Cu_2O and CuO show that Cu_2O is not a purely ionic crystal and that covalent bonding is important in CuO. The large value of $(\partial \ln \nu_Q/\partial \ln P)_T$ found for CuO suggests that meaningful measurements of $(\partial \ln \nu_Q/\partial P)_T$ can be made below 10 kbar for the high T_c superconductors, despite their greater NQR linewidths, and that such measurements will prove a stringent test of models of the valence states and bonding in these materials.

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