Temperature Dependence of Nuclear Quadrupole Resonance in Cuprous Oxide*

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The pure nuclear quadrupole resonance frequencies of ^{63}Cu and ^{65}Cu nuclei in Cu_2O have been measured from 350 down to 4°K. Below 140°K the dependence deviates from linearity. A model based on vibrations of the Cu nuclei transverse to the O-Cu-O axis is shown to be consistent with the experiments. The frequency ω of the transverse vibrational band is derived to be 97 ± 7 cm^{-1}.

1. INTRODUCTION

THE lattice of Cu_2O has the cuprite structure.[1] Each oxygen is tetrahedrally surrounded by four copper nearest neighbors, while each copper is sandwiched between two oxygens at equal distance. The unit cell is cubic with $a=4.269$ Å; the nearest Cu-O distance is 1.85 Å. The lattice is considered to be ionic.

Nuclear quadrupole coupling in an ionic lattice is usually described in terms of the ionic point model and antishielding: The ions surrounding the Cu ion are considered to be point charges at the lattice positions, and the total electric-field gradient produced at the site of the Cu nucleus is amplified by quadrupolar polarizations[2] in the Cu ion. In fact, calculations by Bersohn[3] showed that the order of magnitude of the electric-field gradient q at the Cu nucleus can be explained with antishielding and the ionic point model of a *rigid* lattice. Kushida, Benedek, and Bloembergen,[4] studying effects of pressure, found a linear dependence of q on the volume, which is in agreement with the antishielding model.

Recently it has been shown[5] that at certain nuclei in ionic compounds another mechanism of nuclear quadrupole coupling must be present because of the short-range repulsive forces between the ions, which balance the Coulomb attraction. This mechanism is however mainly operative in negative ions; Cu in Cu_2O is expected to be an example of pure antishielding.

In the present paper the antishielding model will be used to discuss the influence of *vibrations* of the lattice on the electric field gradient.

2. EXPERIMENTAL

The pure nuclear quadrupole resonance (NQR) frequencies $\nu=\frac{1}{2}e^2qQ$ of ^{63}Cu and ^{65}Cu nuclei (both spin $I=\frac{3}{2}$) have been measured from 350 down to 4°K. The sample in the form of a powder was placed in a radio-frequency coil, which is part of a super-regenerative oscillator of the type described by Dean.[6] The frequency was measured by means of a Hewlett Packard 4245L frequency counter. Frequency modulation at 400 cps as well as Zeeman modulation[7] at 60 cps were employed. The results are presented in Fig. 1, in which also the results of Kushida *et al.*[4] have been included. The linewidth was of the order of 20 kc/sec, and was not found to vary considerably throughout the temperature range.

3. DISCUSSION

The temperature dependence of the electric-field gradient results from thermal vibrations of the lattice.[8] Let q_0 be the electric field gradient in a rigid lattice with the exclusion of even zero-point vibrations. The deviation, due to a certain normal mode of the lattice vibration, of q from q_0 is to first order proportional to the square of the amplitude of that mode. The deviation is consequently proportional to the energy of the corresponding quantum-mechanical oscillator with angular frequency ω_i. That is,[4]

$$q(T)=q_0\left\{1+\sum_i\left[(b_i\hbar\omega_i/k)\times\left(\frac{\exp(\hbar\omega_i/kT)}{1-\exp(\hbar\omega_i/kT)}+\frac{1}{2}\right)\right]\right\}, \quad (1)$$

where the summation extends over all normal modes of vibration. The coefficients b_i are determined by the crystal structure and the particular mode, but are independent of the temperature.

Let us now consider the electric field gradient q at the site of the Cu nucleus in Cu_2O. Because of the $1/r^3$ dependence of q and the high symmetry of the crystal (the Cu ions do not contribute to q since they form a fcc

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[8] The thermal expansion coefficient of Cu_2O is small: 2×10^{-6} °K^{-1} (see Ref. 9). As a consequence the NQR temperature dependences at constant volume and constant pressure differ by a few percent only.

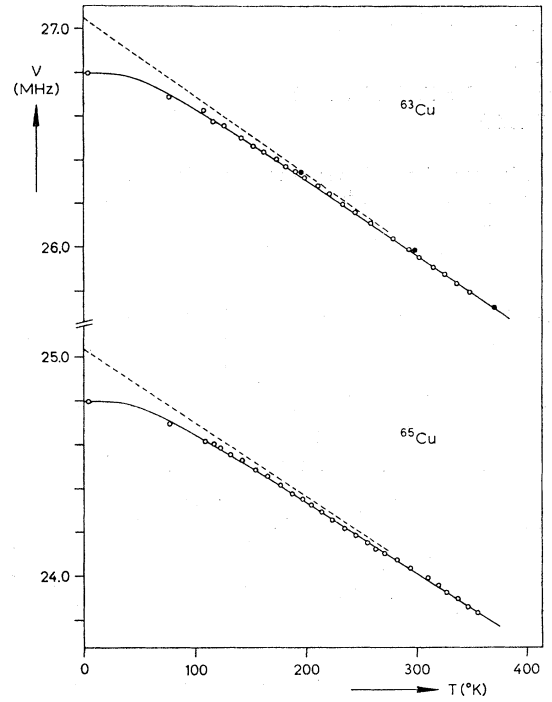

FIG. 1. The pure NQR frequencies of ^{63}Cu and ^{65}Cu in Cu_2O as a function of temperature. The solid curves represent the theoretical Eq. (2) with the values of Table I. The dashed lines are the classical asymptotes, Eq. (3). The black circles denote the results of Kushida *et al.* (see Ref. 4).

lattice), the major part of q is produced by the two adjacent oxygen ions. The temperature dependence even falls down with $1/r^5$ [see Eq. (4)]. In calculating an order of magnitude it is therefore sufficient to consider the motion of the Cu nucleus with respect to the nearest oxygen neighbors only. The summation then can be simplified substantially. Firstly, the effects of normal modes associated with stretching of the Cu-O bonds can be neglected with respect to the effects of bond bending modes. The reasons for this are that the effect of a particular mode is proportional to the square of the relative nuclear displacements, and that these displacements are many times smaller in stretching modes than in bending modes. Secondly, because the O-Cu-O axis is a threefold axis of symmetry, there is a degenerate vibrational band associated with motions of the Cu nucleus transverse to the axis. It will be assumed that all of the frequencies associated with this doubly degenerate band are close to ω. The summation now reduces to

$$\nu(T)=\nu_0\left[1+(b\hbar\omega/k)\left(\frac{\exp(\hbar\omega/kT)}{1-\exp(\hbar\omega/kT)}+\frac{1}{2}\right)\right], \quad (2)$$

where b stands for the sum of the b_i over the modes of the transverse vibrational band. The constants ν_0, b, and ω in Eq. (2) have been adjusted to the experimental data

TABLE I. The rigid-lattice NQR frequency ν_0, the relative temperature dependence b at constant pressure, and the frequency ω of the transverse vibrational band.

	^{63}Cu	^{65}Cu
ν_0 (Mc/sec)	27.046±0.010	25.029±0.010
b (°K^{-1})	$-(1.31\pm0.01)\times10^{-4}$	$-(1.30\pm0.01)\times10^{-4}$
ω/c (cm^{-1})	97 ±7	96 ±7

of both ^{63}Cu and ^{65}Cu. The results are given in Table I, and are plotted as the solid curves in Fig. 1. At temperatures higher than $\hbar\omega/k(=140°K)$ Eq. (2) approaches asymptotically to the classical expression

$$\nu(T)=\nu_0(1+bT), \quad (3)$$

which is drawn as the dashed curves in Fig. 1.

We finally show that the model of a degenerate vibrational band is consistent with the measured temperature dependence. Averaging of the electric-field-gradient operator $(3\cos^2\theta-1)/r^3$ over the transverse vibration, while the Cu-O distances are preserved, yields the result that the transverse band produces to first order a variation according to

$$q=q_0(1-3x_0^2/4R^2), \quad (4)$$

in which x_0 is the vibrational amplitude of the Cu nucleus relative to the O-Cu-O axis and R is the Cu-O distance. From Eqs. (3) and (4) we have at high temperatures

$$b=-3x_0^2/4R^2T. \quad (5)$$

It is noted that the effect of transverse vibrations is negative in contrast to the (neglected) effect of stretching vibrations. We take from Table I $\omega/c=97$ cm^{-1}. From x-ray studies[9] an average rms nuclear displacement of 0.26 Å at 300°K has been derived. With Eq. (5) it is concluded that b is of the order of 10^{-4} °K^{-1}, which is comparable with the experimental value.

4. CONCLUSIONS

It has been shown that measurements on the temperature dependence of nuclear quadrupole resonance at sufficiently low temperatures makes possible a determination of the frequencies of lattice vibrations with wavelength comparable with the nearest-neighbor distance. In cuprous oxide the vibrational band associated with motion of the Cu nuclei transverse to the O-Cu-O axis has been identified. In addition, the results substantiate the antishielding model for nuclear quadrupole coupling at the Cu nucleus, and support the conclusion that cuprous oxide has the ionic structure.

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