Anomaly of Nuclear Quadrupole Relaxation in Cu_2O Prepared at Low Temperatures*

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The ^{63}Cu and ^{65}Cu NQR transitions in powder samples of cuprous oxide have been investigated from 77 to 500 K and at room temperature after annealing up to 1100 K. Significant differences in T_1, NQR linewidth $\Delta\nu$, and their temperature dependences were found among the samples prepared in different ways. For Cu_2O samples obtained in low temperatures (below 380 K), the temperature dependence of T_1 below 380 K is of activation character with $E_a = 0.07$ eV. These results are interpreted in terms of an electron hopping mechanism. Thermal processing of these samples permits to obtain irreversible electronic state and then the spectroscopic parameters are the same as for the samples obtained in high temperatures (above 1320 K).

1. Introduction

Cuprous oxide Cu_2O is known to be a metal-deficient p-type semiconductor with cation vacancies and electron holes as the primary defects [1]. The Cu_2O unit cell is cubic and contains two molecules. The copper atoms have two oxygen-atom neighbours at equal distances; each oxygen atom is surrounded tetrahedrally by four coppper atoms.

The deviation from stoichiometry has been studied as a function of temperature and oxygen partial pressure by several authors [1–3], but mostly for samples obtained at high temperatures. The semiconductor and other properties were depending on the thermal history of the samples. An NQR investigation was undertaken of Cu_2O and high both at low temperatures (LT-Cu_2O) and high temperatures (HT-Cu_2O).

2. Experimental

LT-Cu_2O samples were obtained by precipitation of Cu_2O from an aqueous solution of cupric sulfate $CuSO_4 \cdot 5\,H_2O$ and glucose with sodium hydroxide NaOH [4, 5]. The reaction was performed at 307 K. The precipitate was dried in vacuum at temperatures below 380 K. HT-Cu_2O samples were obtained by oxidation of copper foil [6]. A foil of 99.99% purity and 0.1 mm thickness was obtained from BDH. The oxidation was carried out under atmospheric pressure at 1320 K, and the foil was then ground in an agate mortar.

The samples were subjected to an X-ray investigation using the Bragg-Brentano method with monochromatized CuK_α radiation. The diffraction patterns proved that the symmetry and elementary cell parameters of the LT and HT samples were identical.

Quadrupole relaxation times T_1, frequencies ν_Q and linewidths for ^{63}Cu and ^{65}Cu were investigated by a RADIOPAN pulse NQR spectrometer PS-1-50 [7, 8]. In order to improve the signal-to-noise ratio and signal registration, we used a two-channel boxcar integrator with a digital memory. High stability of the pulse duration, pulse intervals and sequence repetition period was ensured by a programmed digital generator enabling automatization of the measurements.

The Cu_2O samples to be investigated were sealed in glass vials and placed in the transmitter-receiver coil of the spectrometer. Measurements were performed under atmospheric pressure and under 0.01 Pa. Automatic temperature control secured long-term stability to within ± 0.1 K.

For comparison of the results obtained by pulse-techniques, additional measurements of the line-

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width were performed by a superregenerative spectrometer with digital sweep of frequency and antisymmetric modulation [9].

3. Results

The NQR spectra of both HT- and LT-cuprous oxide for both ^{63}Cu and ^{65}Cu consist of a single line. NQR parameters for ^{63}Cu in LT- and HT-samples are given in Table 1 together with values of the magnetic susceptibility χ. The frequencies ν_Q differ only slightly for LT and HT and are linear functions of the temperature (Figure 1). However, the linewidth as well as T_1 are significantly different for LT- and HT-samples (Table 1). For LT samples, T_1 was found to decrease rapidly with increasing temperature up to 380 K and then to increase irreversibly to just the same value as for HT samples

Table 1. NQR parameters for LT- and HT-Cu_2O.

Parameter	LT-Cu_2O	HT-Cu_2O
ν_0 [MHz]*	27.01 ± 0.02	26.99 ± 0.02
$b \times 10^4$ [K^{-1}]*	1.28 ± 0.02	1.27 ± 0.02
$\Delta\nu$ [kHz]	21 ± 2	10.5 ± 1
$T_1(^{65}Cu)/T_1(^{63}Cu)$ [$T = 300$ K]	1.28 ± 0.10	1.28 ± 0.10
$T_1(^{63}Cu)$ [ms] ($T = 300$ K)	27 ± 1	125 ± 4
$\chi \times 10^9$ [$m^3\,kg^{-1}$]	1.5 ± 0.1	−0.15 ± 0.04

* From the KBB equation [10] approximated in a linear form; $\nu_Q(T) = \nu_0(1 - bT)$.

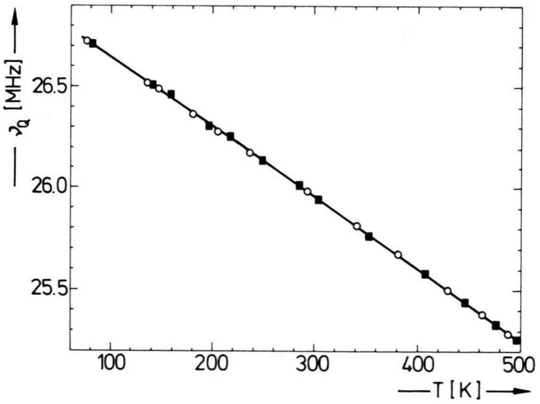

Fig. 1. Temperature dependence of the ^{63}Cu NQR line frequency for LT-Cu_2O. ○ heating, ■ cooling.

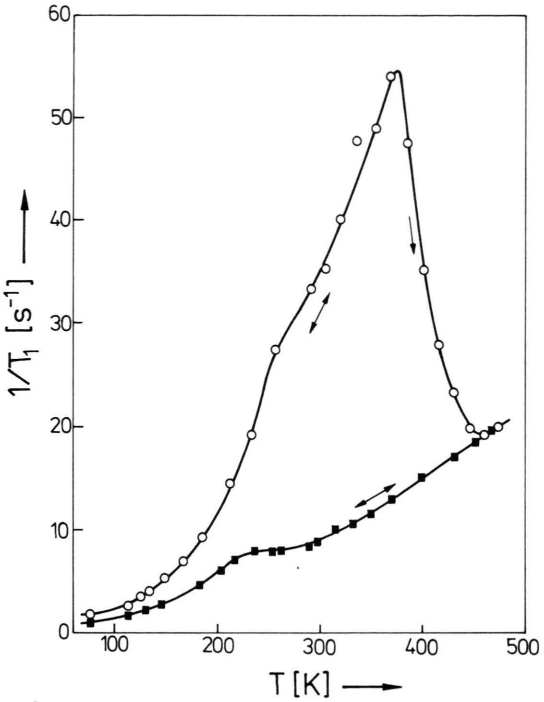

Fig. 2. Temperature dependence of the ^{63}Cu spin-lattice quadrupole relaxation time for LT-Cu_2O.

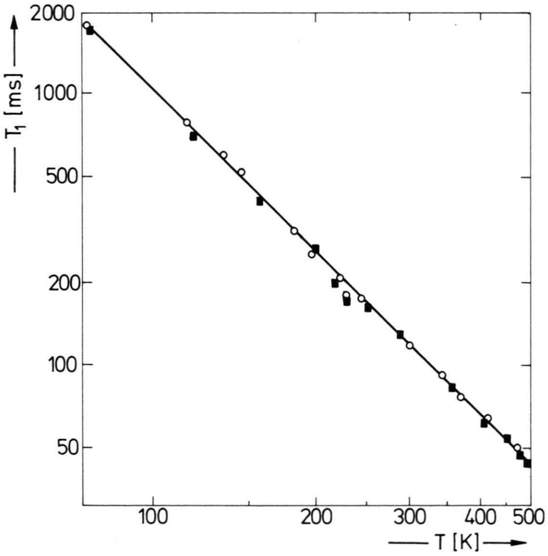

Fig. 3. Temperature dependence of the ^{63}Cu spin-lattice quadrupole relaxation time for HT-Cu_2O samples. ○ heating, ■ cooling.

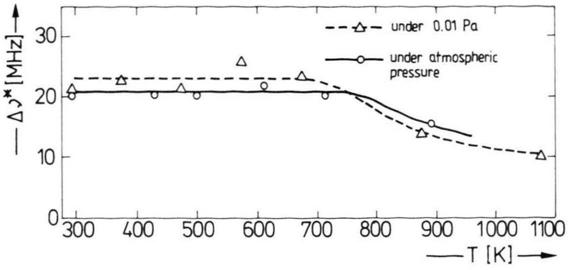

Fig. 4. Dependence of the ^{63}Cu NQR linewidth for LT-Cu_2O on the annealing temperature (annealing time = 0.5 h).

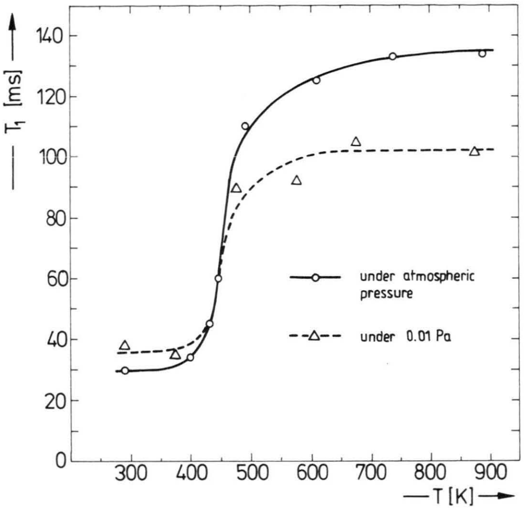

Fig. 5. Dependence of ^{63}Cu spin-lattice relaxation time for LT-Cu_2O on the annealing temperature (annealing time = 0.5 h).

(Figure 2). The temperature dependence of T_1 for HT samples is shown in Figure 3.

When LT-Cu_2O is annealed at a temperature higher than 900 K, its spectroscopic parameters become the same as those of an HT sample. Only a slight influence of air pressure on $\Delta\nu$ and T_1 was observed (Fig. 4 and Figure 5).

Moreover, LT samples obtained below 380 K were carmine in colour, those annealed above 400 K were dark brown, and those annealed at 1100 K were bright pink.

4. Discussion

Although the two kinds of oxide are crystallographically identical, different values and the temperature changes of $\Delta\nu$ and T_1 have been found. In the case of HT oxide, the T_1 changes can be described by a Raman process ($T_1 \sim a T^{-2}$) [11, 12]. In LT-Cu_2O, an additional relaxation mechanism of activation character with $E_a = 0.07$ eV has been observed (E_a was calculated from $T_1^{-1} - a' T^2 = b \exp(-E_a/RT)$ where the small diviation at about 240 K was neglected). This value of E_a and the reproducibility of the T_1 changes below 380 K, allow us to suppose that an anomalous increase in the quadrupole reelaxation rate with increasing temperature in LT-Cu_2O results from thermal excitations of the electrons related to the charge states, due to autodefects in its crystal lattice. These defects generate local energy levels in the forbidden energy gap, and through them electron hopping may be realized. This movement of charge causes time dependent fluctuations of the electric field gradient (EFG) at the position of the resonating nuclei and becomes an effective mechanism of relaxation. A purely quadrupolar mechanism of relaxation is confirmed by the $T_1(^{65}\mathrm{Cu})/T_1(^{63}\mathrm{Cu})$ ratio comparable with the ratio of the squares of the quadrupolar coupling constants (Table 1), whilst for purely magnetic relaxation the value of this ratio is 0.88 [12, 13].

The NQR investigation does not allow us to determine the kind of defects in Cu_2O. Additional EPR investigations (to be published) have proved the presence of centres claimed to be Cu^{2+} in LT samples which disappear above 430 K where an additional narrow EPR line was observed. Its intensity increases with temperature reaching a maximum at about 600 K; the line disappeared after annealing above 900 K. The line was identified as being due to a paramagnetic centre O^-. Thus we have $Cu^{2+} + e \rightarrow Cu^+$. When the Cu^{2+} EPR signal is quenched, a transfer of electrons from O^{2-} to this centre by thermal excitation occurs. This interpretation is clearer here because charge states of the two ions can both be observed with EPR.

On the grounds of the investigations performed, we propose the following model of lattice defects in the LT-Cu_2O. At low temperatures, in the forbidden energy gap there are local acceptor levels produced by Cu vacancies and filled electron traps in the form of O^{2-} ions. The excited states with Cu^{2+} paramagnetic centres may be obtained by producing cuprous oxide at low temperature or by optical pumping of HT-Cu_2O at a low temperature.

The electron traps are stable up to 380 K. Within this range of temperatures electron hopping takes place with the electron mobility increasing with temperature (at $E_a = 0.07$ eV, also in [1]). Above the characteristic temperature of 380 K, the centres are restructered, Cu^{2+} disappears and electrons are partially released form the traps according to: $O^{2-} \rightarrow O^- + e$. As a consequence, the electron hopping irreversibly disappears and the temperature dependence of T_1 is described by a Raman process.

Above 400 K, a small part of the Cu_2O is oxidized to CuO (a change in colour of the sample but not in the intensity of NQR line was observed) which results in great disorder in the crystal lattice. This is evidenced by the broadening of the NQR line ($\Delta\nu = 21$ kHz). At 900 K (O^- centres disappear) the number of the defects of Cu_2O lattice decreases, which may be concluded from the significant narrowing of the NQR line.

The density of states accessible for electron hopping necessary to produce en effective relaxation mechanism was estimated by the Reif and Torrey method [13–15] to be about 10^{20} cm^{-3}. This value proves a significant concentration of defects but is not in contradiction with the results of the other studies. The results obtained, as well as the estimation of the concentration of defects in LT-Cu_2O are consistent with the results of investigations of the photomemory effect [16, 17], Hall effect [18], and diffusion of point defects [19, 20].

5. Conclusion

The results of the NQR investigations on Cu_2O, in the particular the nuclear quadrupole relaxation time T_1 and linewidth $\Delta\nu$, allow a determination of the charge states and their dynamics. The low value of the activation energy as well as the reversibility of the T_1 changes with temperature in the case of LT-Cu_2O below 380 K suggest that electron hopping is a reasonable relaxation mechanism.

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