Ionic Diffusion in Cu_6PS_5Br Studied by ^{63}Cu NMR

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Applying ^{63}Cu NMR technique, we observed exchange between the nonequivalent copper sites in crystalline Cu_6PS_5Br, known as a member of the mineral "argyrodite". Below 200 K, where the motion of the copper(I) ion is slow, we could distinguish several nonequivalent copper sites. On increasing the temperature, the chemical exchange between the nonequivalent cation sites was seen on the ^{63}Cu NMR spectra. We could determine the activation energy for this motion to be 35 kJ mol^{-1}, in good agreement with the published ionic conductivity.

Key words: Ionic conductor; ^{63}Cu NMR; Quadrupole interaction.

Introduction

Compounds of the formula M_6PS_5X (M = Ag, Cu; X = Cl, Br, I) belong to the mineral "argyrodite" and are known as a new family of acentric structures. The argyrodites have a high-temperature structure of space group F43m [1]. The typical architecture consists of a frame work of interpenetrating distorted icosahedra forming a tetrahedrally packed sublattice, similar to the metal frame work in the Laves phase $MgCu_2$ (Figure 1). These materials have recently attracted much interest [1–10] because of their unique physical and chemical properties, e.g., photointercalation [8–10]. Incomplete occupancy of certain cation sites leads to a high ionic conductivity in various compounds [1–3] and order-disorder phenomena accompanied by structural phase transitions [1, 2, 5]. In an X-ray diffraction study [4], the presence of the six nonequivalent Cu sites was proposed, and the cationic conduction was suggested to take place via Cu^+ ion exchange between nonequivalent sites. Hereafter, we will call the six nonequivalent Cu sites as Cu(i) (i=1 to 6) according to [4].

In order to obtain insight into the ionic conduction mechanism in this system, we performed temperature dependent ^{63}Cu NMR measurements on Cu_6PS_5Br.

Experimental

Cu_6PS_5Br was synthesized by heating a stoichiometric mixture of reagent grade Cu, CuBr, P, and S (Nacalai Tesque Co.) to 300 °C for one hour, and then up to 700 °C for several days in an evacuated quartz tube [2, 3]. The obtained red fine crystals were suspended and washed in ammonia water and then in hydrochloric acid to eliminate CuBr and Cu_2S. The samples were identified by X-ray powder diffraction.

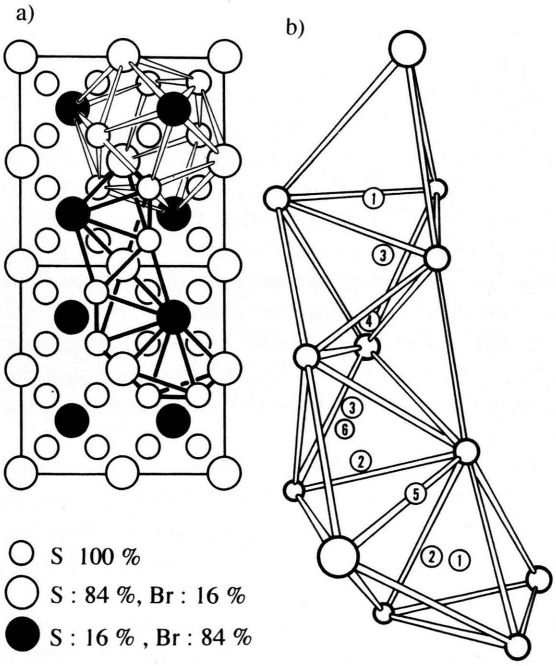

Fig. 1. The schematic representation of the crystal structure of Cu_6PS_5Br. a) Only the anion sublattice is shown. b) Copper ions, numbered 1 to 6, reside at the center, edge, and face center of the tetrahedra formed by anions.

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A small amount of impurity, probably Cu_2S, was detected.

The ^{63}Cu NMR spectra were measured with a Bruker MSL-400 spectrometer at a Larmor frequency of 106.60 MHz. The temperature was controlled within ± 1 K, using a VT-1000 temperature control unit. To obtain the 2D nutation NMR spectra [11], the rf pulse length was increased from 0 to 306 μs every 1.2 μs, and the free induction decay signal after each pulse was sampled. The acquired data were Fourier transformed after zero-filling up to 1024 words in the F_1 dimension. The ^{63}Cu spin-lattice relaxation time, T_1, was also measured by the saturation recovery method, using a Bruker MSL-300 spectrometer at a Larmor frequency of 79.58 MHz.

Results and Discussion

Our NMR measurements were carried out in the temperature range between 183 and 400 K, in which no phase transition was detected in our study of differential scanning calorimetry (DSC), although phase transitions at 178 K, observed by differential thermal analysis, [2], and at ca. 230 [3] and 257 K [5], observed by DSC, were reported.

The ^{63}Cu NMR spectrum of Cu_6PS_5Br at 183 K is shown in Figure 2. The length of rf pulse which gave the maximum signal intensity was nearly half that of the ^{63}Cu signal in CuCl having almost zero quadrupole interaction. This means that the observed spectrum corresponds to the "central" transition not shifted by first order quadrupole interaction. This spectrum tells us that there are at least four nonequivalent copper sites in the crystals and is consistent with the X-ray diffraction study [3], although we could not attribute the observed peaks to the nonequivalent Cu sites reported.

The contour plot of the ^{63}Cu 2D nutation NMR spectrum at 185 K is shown in Fig. 3, in which we can distinguish three kinds of nonequivalent sites from the pattern along the vertical (F_1) direction. At this temperature, we can safely assume that the Cu ions are statistically distributed between the noneqiuvalent sites, since the observed spectrum consists of several distinguishable peaks. As for the sites numbered 2, 3 and 4, we could determine the quadrupole coupling constant (e^2Qq) and the asymmetry parameter of the electric field gradient (EFG) tensor (η) in the following manner. We compared experimental and calculated

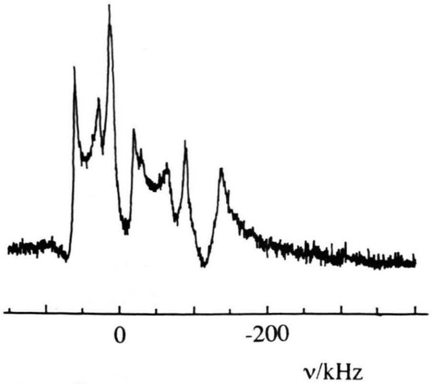

Fig. 2. ^{63}Cu NMR spectrum observed at 185 K. At least four nonequivalent Cu sites are seen in the spectrum.

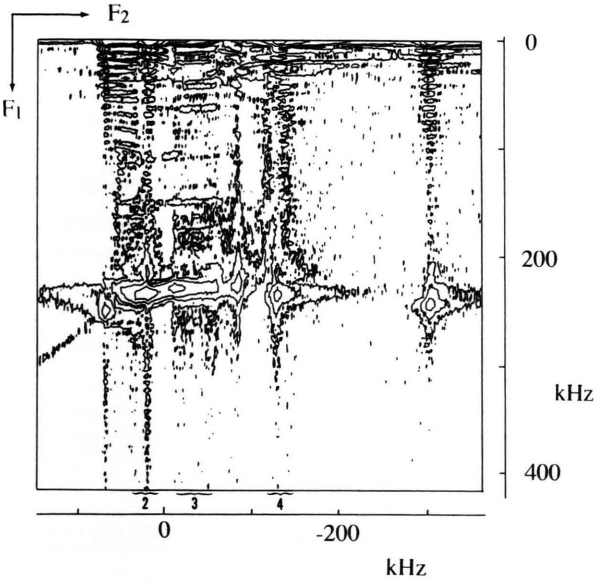

Fig. 3. The contour plot of the 2D nutation NMR spectrum at 185 K. The peaks marked by the brackets could be attributed to nonequivalent copper sites in the crystal because of the difference in the pattern along the vertical (F_1) direction.

Table 1. The obtained (left) and calculated (right) quadrupole parameters of the six nonequivalent Cu sites. The calculated EFG values are relative to the maximum.

Site	e^2Qq/h (MHz)	η	eq/eq_{max}	η
Cu(1)	–	–	1.00	0.1
Cu(2)	3.6	0.0	0.40	0.4
Cu(3)	6.3	0.2	0.57	0.2
Cu(4)	6.1	0.9	0.38	0.9
Cu(5)	–	–	0.33	0.9
Cu(6)	–	–	0.45	0.8

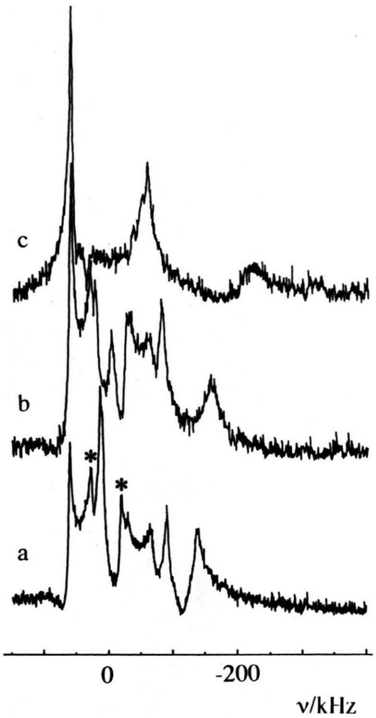

Fig. 4. The temperature dependence of ^{63}Cu NMR spectrum at low temperatures. a) 185 K, b) 200 K, c) 220 K. Note that the peaks marked by the asterisks gradually lose their intensity on heating.

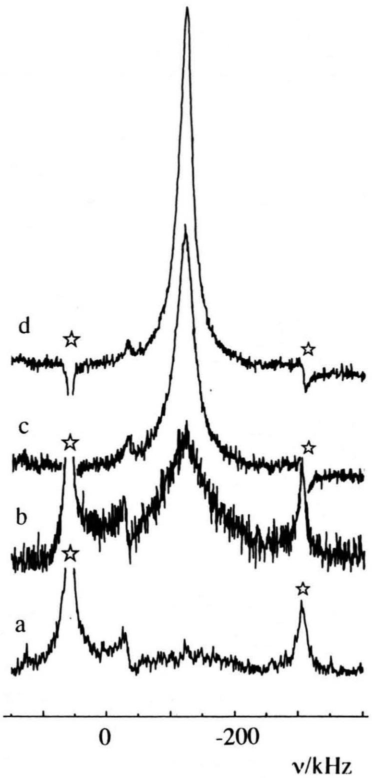

Fig. 5. The temperature dependence of ^{63}Cu NMR spectrum at high temperatures. a) 315 K, b) 330 K, c) 345 K, d) 360 K. A single line was narrowed on heating. The peaks shown by the asterisk are due to impurities.

patterns along the F_1 and F_2 directions, in which the latter pattern corresponds to the normal 1-D spectrum, to get consistent results. The parameters derived here, and the EFG values calculated by the method reported in [12], are given in Table 1. The calculated EFG was obtained by assuming that the Cu^+ ion is stochastically distributed between the sites, i.e., the given site "sees" the averaged charge of the neighbours. By comparing the relative spectrum intensities and asymmetry parameters, the sites corresponding to $e^2 \partial q$ values are assigned to Cu(2), Cu(3), and Cu(4), as indicated in Figure 3.

On increasing the temperature, we observed the gradual change in the 1-D spectrum shown in Figs. 4 and 5. The peaks indicated by the asterisks in Fig. 4 gradually lost their intensity on heating, and finally all peaks were buried in the noise around 240 K. This means that, on heating, the exchange rate between the two sites marked by the asterisks becomes comparable to the frequency difference of the two, and then all copper sites become exchangeable. We evaluated the spin-spin relaxation time T_2^* defined by $\Delta\nu^{-1}$, where $\Delta\nu$ is the full width at the half-maximum. This T_2^*, which gives the averaged or apparent correlation time of the exchange motion, is plotted against the inverse temperature in Figure 7. The slope gives an activation energy of 35 ± 6 kJ mol^{-1}, which is compatible to the 36 kJ mol^{-1} determined by the conductivity measurements [1].

We also measured the ^{63}Cu spin-lattice relaxation time for the central transition in the temperature range 310–355 K, where a single ^{63}Cu line was observed. The determined temperature dependence of T_1 is shown in Figure 6. We evaluated the activation energy to be 11 ± 3 kJ mol^{-1}, which is small compared with those obtained from T_2^* and conductivity measurements. This difference is explainable as follows. In the T_2^* measurement, we observed the averaging pro-

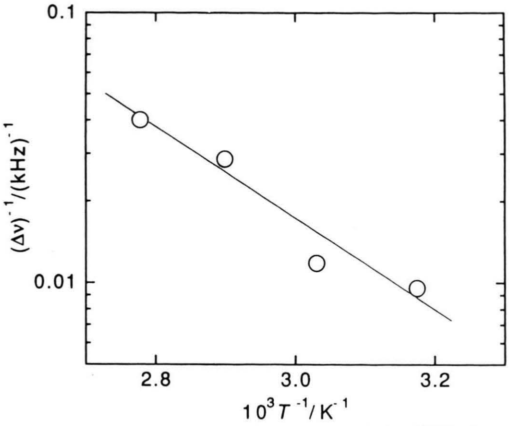

Fig. 6. The temperature dependence of the ^{63}Cu NMR spin-lattice relaxation time (T_1). The slope of the best fitted solid line gives an activation energy of 11 kJ mol^{-1} for the local exchange motion of the Cu^+ ions.

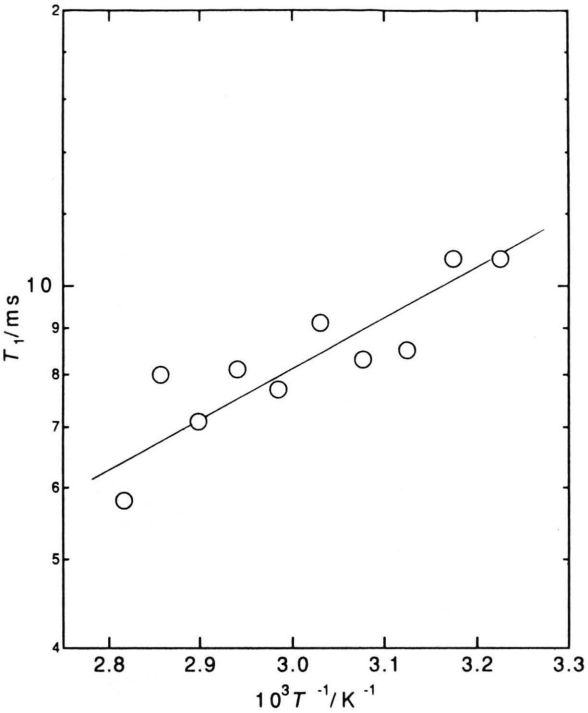

Fig. 7. The inverse line width $\Delta\nu$ vs. inverse temperature. The slope of the best fitted solid line in the figure gives an activation energy of 35 kJ mol^{-1} for the exchange motion of the Cu^+ ions.

cess of the quadrupole interaction by the exchange motion among all nonequivalent sites. Since motions in the order of 10^5 Hz are effective to T_2^*, but those of 10^8 Hz contribute to T_1, the motion shortening T_2^* gives no appreciable contribution to T_1, if it is slow. On the other hand, the T_1 process governed by the local exchange between e.g. Cu(2) and Cu(3) sites, which may be fast enough, can cause more effectively the spin-lattice relaxation.

Conclusion

We could observe the occurrence of the exchanging motion between the nonequivalent copper sites in Cu_6PS_5Br. Below 200 K the motion of the cation is negligible and we could distinguish several nonequivalent copper sites. On increasing the temperature, the exchange motion among all nonequivalent sites could be seen the ^{63}Cu NMR spectra. We determine the activation energy for this motion to be 35 ± 6 kJ mol^{-1}, which agrees well with the result from the conductivity measurements.

[1] W. F. Kuhs, R. Nitsche, and K. Scheunemann, Mat. Res. Bull. **14,** 241 (1979).
[2] W. F. Kuhs, R. Nitsche, and K. Scheunemann, Mat. Res. Bull. **11,** 1115 (1976).
[3] S. Fiechter, J. Eckstein, and R. Nitsche, J. Cryst. Growth **61,** 275 (1983).
[4] W. F. Kuhs, R. Nitsche, and K. Scheunemann, Acta Crystallogr. B **34,** 64 (1978).
[5] S. Fiechter and E. Gmelin, Thermochimica Acta **85,** 155 (1985); **87,** 319 (1985).
[6] E. Gmelin and R. Villar, Physica **108 B,** 1003 (1981).
[7] J. Shamir, S. Fiechter, and H. Wetzel, J. Raman Spectr. **17,** 217 (1986).
[8] G. Betz, H. Tributsch, and S. Fiechter, J. Electrochem. Soc. **131,** 640 (1984).
[9] T. M. Batirov, V. M. Fridken, R. Nitsche, and K. A. Verkhovskaya, Phys. Stat. Sol. (a) **72,** K 105 (1982).
[10] A. Bubenzer and R. Nitsche, J. Appl. Cryst. **11,** 152 (1978).
[11] A. Samoson and E. Lippmaa, Chem. Phys. Lett. **100,** 203 (1983); Phys. Rev. B **28,** 6567 (1983).
[12] H. Nakayama, T. Eguchi, and N. Nakamura, Z. Naturforsch. **45 a,** 375 (1990).