The Lowest-Temperature Phase Transition of the Mixed Crystal of $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ and the Reorientation of Ammonium Ions in the Crystals

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With decreasing temperature, the mixed crystal $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ at low potassium concentrations yields four solid phases, I, II, III, and IV. With increasing potassium concentration, the phase transition between III and IV disappears. By DTA, the corresponding transition temperature T_c was measured as a function of x. The mechanism of the phase transition is discussed, considering the reorientational motion of ammonium ions. The activation energy of (3 ± 1) kJ mol^{-1} for the motion of the ammonium ions obtained from our model agrees well with the experimental value of (2 ± 0.5) kJ mol^{-1} for the same motion in diamagnetic $(NH_4)_2Cd_2(NO_2)_6$, which was studied as reference compound because its crystal structure is very similar. T_c of $(NH_4)_2Pb[Cu(NO_2)_6]$ increased from 94 to 99 K by deuteration. This isotope effect is well interpreted in terms of the above model.

Introduction

Ammonium lead(II) hexanitrocuprate(II), $(NH_4)_2Pb[Cu(NO_2)_6]$ is known to undergo three phase transitions at 316, 287, and 95 K [1], corresponding to phases denoted by I, II, III, and IV. The complexes of $R_2Pb[Cu(NO_2)_6]$ type with R = K, Rb, Cs, and Tl are well known to show successive phase transitions caused by a cooperative Jahn-Teller effect of $[Cu(NO_2)_6]^{4-}$ ions in a temperature range of 250 K to 390 K and the corresponding phases I, II, and III described as above exist [2–5]. The present complex also shows such phase transitions. However, it is very interesting that another phase transition has been found for this complex at the very low temperature of 95 K and the lowest temperature phase IV exists.

The crystal structure of the phases I, II, and III of $K_2Pb[Cu(NO_2)_6]$ has been extensively studied by ESR [6–8] and diffraction techniques [3]. The highest temperature phase I has cubic symmetry belonging to the space group Fm3 and the intermediate temperature phase II is known to be incommensurate, where the local Jahn-Teller distortion of the complex anions is modulated along the [110] direction. In the phase III there exist two crystallographically nonequivalent $[Cu(NO_2)_6]^{4-}$ octahedra elongated along [100] and [010], as schematically illustrated in Fig. 1, where anions are ordered antiferrodistortively (indicated hereafter as AF-distortive order). The AF-distortive order of elongated $[Cu(NO_2)_6]^{4-}$ octahedra was confirmed to exist in phase III of the ammonium salt from our ESR study [9]. Additionally, our study revealed the appearance of a ferrodistortive (abbreviated as F-distortive) ordered state in the phase IV. The present investigation has been undertaken to clarify the mechanism of the unusual III–IV phase transition and to obtain information about the nature of the phase IV, by determining the transition temperature T_c of $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ as a function of potassium concentration, and the shift of T_c by deuteration. The motion of the ammonium ions was also studied by measuring the ^{1}H NMR spin-lattice relaxation time T_1 in diamagnetic $(NH_4)_2Cd_2(NO_2)_6$ having a very similar structure to that of $(NH_4)_2Pb[Cu(NO_2)_6]$.

Experimental

The homemade DTA apparatus could be used above ca. 20 K with liq. He as a cryogen. A copper-constantan and a chromel-gold (Fe: 0.07%) thermocouple were used as differential and sample temperature thermometers, respectively.

ESR spectra were recorded by use of a JEOL SCXA X-band spectrometer with a TE_{011} cylindrical cavity resonator. An uniaxial goniometer was fixed to the

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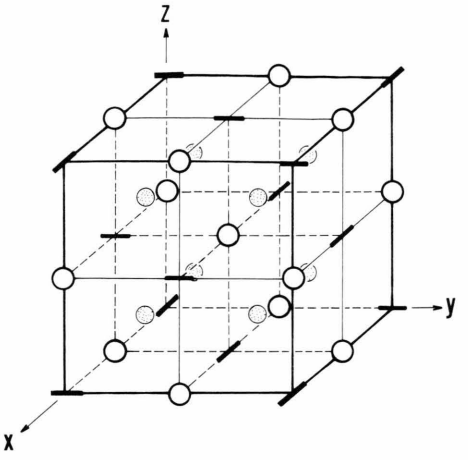

Fig. 1. Antiferrodistortive order of elongated $[Cu(NO_2)_6]^{4-}$ octahedra in $R_2Pb[Cu(NO_2)_6]$ with R = K, Rb, Cs, Tl, and NH_4. Open circles and the circles with dots denote Pb^{2+} and R^+, respectively. The elongated octahedron is represented by a thick bar, the orientation of which coincides with the axis of elongation. The structure is illustrated with reference to the high temperature cubic unit cell. The primitive translation vectors of the lattice shown in this figure are approximately given by $(1/2)[110]_{cubic}$, $(1/2)[011]_{cubic}$, and $(1/2)[1\bar{1}2]_{cubic}$ [3].

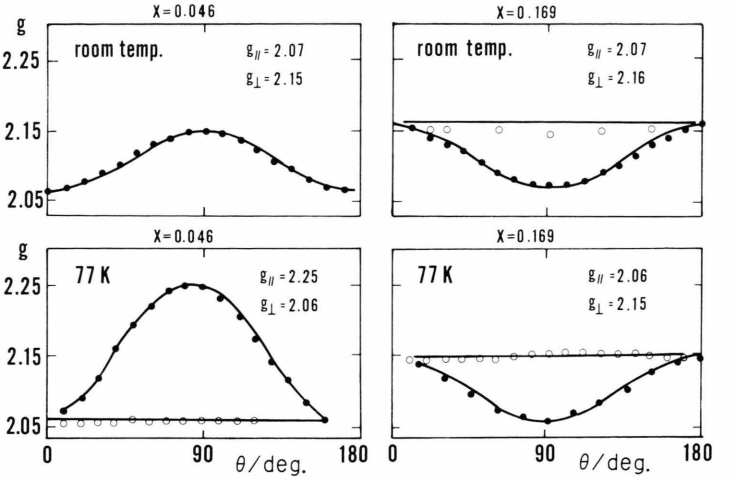

Fig. 2. Angular dependences of the g values observed at room temperature and 77 K for two single crystals of $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ with $x = 0.046$ and 0.169. In general, ESR signals from two different domains can be observed as distinguished by full and open circles. Solid curves are theoretical ones calculated under the assumption of an axially symmetric g tensor with the $g_{||}$ and $g_\perp$ values indicated.

cavity so that the goniometer axis was perpendicular to the external magnetic field. Mn^{2+}/MgO was used as a marker.

A homemade pulsed NMR spectrometer [10] was employed for the determination of ^1H T_1 at the Larmor frequency of 20 MHz, using the usual pulse sequence of $180°-\tau-90°$.

Mixed crystals $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ were prepared by a method described in [11]. A mixture of NH_4NO_3 and KNO_3 was used instead of NH_4NO_3. $(ND_4)_2Pb[Cu(NO_2)_6]$ was obtained by adding a D_2O solution of ND_4Cl, $Pb(NO_3)_2$, and $CuCl_2$ to a D_2O solution of $NaNO_2$ in a dry box filled with N_2 gas. The samples prepared were dried in a desiccator over P_2O_5 and sealed in a glass ampoule for the DTA measurements with a little amount of He as an exchange gas. $(NH_4)_2Cd_2(NO_2)_6$ was synthesized similarly from NH_4NO_3, $Cd(NO_3)_2$, and $NaNO_2$.

The potassium fractions in $(NH_4)_{2(1-x)}K_{2x}$-$Pb[Cu(NO_2)_6]$ were determined by the so called mercuric chloride method using sodium tetraphenylboron as a precipitating reagent [12–14]. For the analysis, the sample was dissolved in a dilute HNO_3 solution in a teflon beaker. Then, a solution of potassium free NaOH (Merck, K < 0.0002 wt%) was added. The resultant solution was heated nearly to dryness over a water bath to remove NH_3. The residue was dissolved in acetic acid, and the pH of the solution was adjusted to 4.5 by use of CH_3COONa. Finally, potassium was precipitated as $K[(C_6H_5)_4B]$ by adding an $Na[(C_6H_5)_4B]$ solution.

Results

The angular dependence of the g values was observed at room temperature and 77 K for two kinds of the single crystal of $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ with x equal to 0.046 and 0.169. The results are shown in Figure 2. A tetragonal shaped crystal was rotated about the axis perpendicular to the square basal plane. The crystal lattice axes were deduced from the morphology of the crystal employed and the angular dependence curves of the ESR spectra observed.

The phase transition temperatures determined by DTA measurements with increasing temperature are listed in Table 1. $T_{tr}(II \rightarrow I)$ and T_c showed a fairly

Table 1. Phase transition temperatures $T_{tr}(II \rightarrow I)$, $T_{tr}(III \rightarrow II)$, and T_c determined by DTA measurements for $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ and $(ND_4)_2Pb[Cu(NO_2)_6]$. The mole fraction of potassium determined by chemical analysis is indicated by x.

Compounds	x	$T_{tr}(II \rightarrow I)$/K	$T_{tr}(III \rightarrow II)$/K	T_c/K
$(ND_4)_2Pb[Cu(NO_2)_6]$	–	310 ± 1	280 ± 7	99 ± 1
$(NH_4)_2Pb[Cu(NO_2)_6]$	–	315 ± 2	286 ± 1	94 ± 1
$(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$	0.046 ± 0.002	314 ± 2	287 ± 1	90 ± 2
	0.096 ± 0.002	312 ± 1	287 ± 1	83 ± 3
	0.099 ± 0.009	312 ± 1	287 ± 1	81 ± 2
	0.169 ± 0.002	311 ± 2	286 ± 1	77 ± 3
	0.187 ± 0.002	308 ± 1	286 ± 1	65 ± 10
	0.204 ± 0.002	308 ± 1	286 ± 1	64 ± 6
	0.216 ± 0.003	308 ± 1	286 ± 1	60 ± 9
	0.228 ± 0.002	307 ± 1	285 ± 1	56 ± 9
	0.276 ± 0.002	304 ± 1	285 ± 1	–

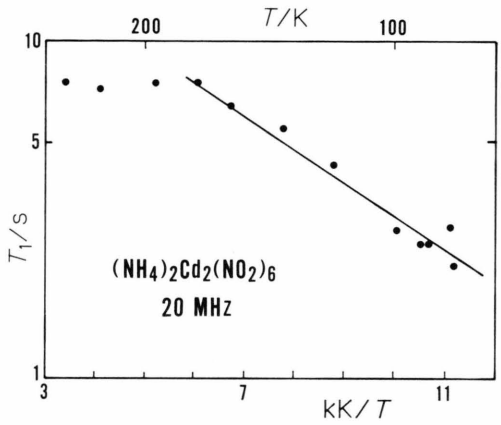

Fig. 3. Temperature dependence of ^1H T_1 observed at the Larmor frequency of 20 MHz for $(NH_4)_2Cd_2(NO_2)_6$.

large decrease with increasing x, whereas $T_{tr}(III \rightarrow II)$ was almost independent of x. For the sample doped with potassium, broad heat anomalies were recorded for the transition III–IV, where the peak temperatures of the anomalies were assigned as T_c. By deuteration, $T_{tr}(II \rightarrow I)$ and $T_{tr}(III \rightarrow II)$ of $(NH_4)_2Pb[Cu(NO_2)_6]$ were shifted to lower temperatures, while T_c increased by ca. 5 K.

Figure 3 shows a ^1H log T_1 vs. T^{-1} plot observed for diamagnetic $(NH_4)_2Cd_2(NO_2)_6$.

Discussion

The angular dependence of the ESR spectra observed for the phases of $(NH_4)_2Pb[Cu(NO_2)_6]$ can be interpreted by assuming an axially symmetric crystal g tensor with $g_\parallel < g_\perp$ for II and III, and with $g_\parallel > g_\perp$ for IV [9]. From the angular dependence of g shown in Fig. 2 it is clear that $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$ with $x = 0.169$ does not undergo the III → IV phase transition down to 77 K, whereas the crystal with $x = 0.046$ exists in the phase IV at 77 K. This suggests that T_c decreases with increasing x, and this is confirmed by the measurements of DTA, the results of which are listed in Table 1. Since the phase IV with F-distortive cooperative order does not appear for $R_2Pb[Cu(NO_2)_6]$ with a monoatomic ion R^+, the lower symmetry of the NH_4^+ ions is considered to play an important role for the occurrence of the F-distortive structure. At higher temperatures, where the NH_4^+ ions reorient fast enough, NH_4^+ can be approximated as an isotropic free rotor. Accordingly, the AF-distortive structure is realized to be stable at these temperatures. We therefore assume that the IV–III phase transition is strongly related to the reorientation of ammonium ions. Since the crystal structure of III is only slightly distorted from the Fm3 structure [1], there exist 12 nearest-neighbor (n-n) interactions between the $[Cu(NO_2)_6]^{4-}$ octahedra. Among them, the 6 n-n interactions are F-distortive and the others AF-distortive in the AF-structure, as shown in Fig. 1, in the sense that the two axes of elongation for the n-n pairs of the octahedra are parallel or orthogonal for the F- or AF-distortive interaction, respectively. On the other hand, all n-n interactions must be F-distortive in the F-structure which is expected for the phase IV of $(NH_4)_2Pb[Cu(NO_2)_6]$. Here, we assume that the phase transition III → IV, involving the change of the n-n interactions from AF- to F-type, occurs where the correlation time of the reorientation of NH_4^+ ions becomes sufficiently long.

Here, we introduce an energy parameter J which describes a lattice-dynamical coupling between a pair of the octahedral complexes deforming the octahedrons. F-Distortive and AF-distortive n-n interactions are described by positive and negative J values, respectively. In the following discussion, only the 6 n-n interactions which are AF-distortive in the AF-structure are taken into account. For these n-n interactions, we assume $J = J_F > 0$ when the ammonium ion is in a stable orientation and $J = -J_{AF} < 0$ when the cation is describable as a spherical ion.

At a given temperature, the ammonium ion is expected to be in a stable orientation during a resident time τ and in a rotational state within a transient time τ^*. In the NQR [15–17] and neutron scattering [18, 19] studies of the reorientation of ammonium ions, both of a resident and a transient time are usually considered. For this situation, the n-n interactions in question will be described by an averaged parameter given by

$$(\tau J_F - \tau^* J_{AF})/(\tau + \tau^*). \tag{1}$$

Since there exist eight ammonium ions and the 6 n-n interactions in the high temperature unit cell (cubic), the energy parameter per an ammonium ion in the unit cell can be written as

$$(3/4)(\tau J_F - \tau^* J_{AF})/(\tau + \tau^*). \tag{2}$$

By assuming that the phase transition occurs when the energy parameter becomes zero, the following relation is obtained at T_c:

$$\tau = (J_{AF}/J_F)\,\tau^*. \tag{3}$$

For the mixed crystal of $(NH_4)_{2(1-x)}K_{2x}Pb[Cu(NO_2)_6]$, (2) can be modified as follows by taking into account that the above energy parameter is always equal to $-(3/4)J'_{AF}$ per monovalent cation at the site where NH_4^+ is replaced by K^+:

$$(3/4)\{[(1-x)(\tau J_F - \tau^* J_{AF})/(\tau + \tau^*)] - x J'_{AF}\}. \tag{4}$$

Since $J'_{AF} \approx J_{AF}$, we have at T_c

$$\tau = \{J_{AF}/[(1-x)J_F - x J_{AF}]\}\,\tau^*. \tag{5}$$

Here, τ^* is assumed to be independent of temperature, whereas τ varies according to an Arrhenius relationship [16, 17] as

$$\tau = \tau_\infty \exp(E_a/RT), \tag{6}$$

where E_a and τ_∞ denote the activation energy for the reorientation of the ammonium ions and the resident time at the limit of infinite temperature. Putting (6) into (5) and taking logarithms, we have

$$\ln \tau_\infty + (E_a/RT_c) = \ln \tau^* - \ln\{[(1-x)J_F/J_{AF}] - x\}. \tag{7}$$

Similarly, from (3) we have for the pure system

$$\ln \tau_\infty + (E_a/RT_{c0}) = \ln \tau^* - \ln(J_F/J_{AF}). \tag{8}$$

Here, T_{c0} denotes T_c for the pure system. By subtracting (8) from (7), one obtains

$$1 - (T_{c0}/T_c) = \alpha \ln(1 - \beta x), \tag{9}$$

where
$$\alpha = RT_{c0}/E_a, \tag{10}$$

$$\beta = (J_F + J_{AF})/J_F. \tag{11}$$

In the above derivation, we assumed that E_a, J_F, and J_{AF} are independent of the potassium concentration as well as temperature.

Equation (9) was fitted to the observed concentration dependence of T_c, taking α and β as adjustable parameters. Thus E_a and β were obtained as (3 ± 1) kJ mol^{-1} and (4.0 ± 0.4), respectively, using the computer program SALS [20]. The observed T_c and the calculated curve are shown in Fig. 4 as a function of x.

To examine the adequacy of our model, we tried to obtain E_a for the reorientation of the ammonium ions from measurements of ^{1}H NMR T_1. However, very short and almost temperature independent T_1 values of 4 ms were obtained for $(NH_4)_2Pb[Cu(NO_2)_6]$ because of its paramagnetism. Therefore, the temperature dependence of ^{1}H T_1 was studied for $(NH_4)_2Cd_2(NO_2)_6$, which is supposed to have a crystal structure very similar to that of the present

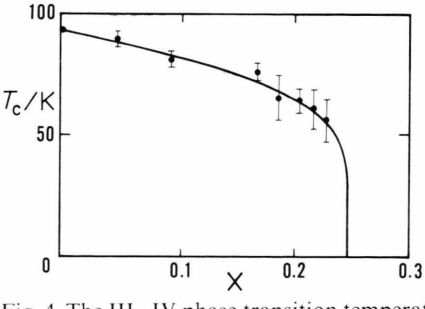

Fig. 4. The III–IV phase transition temperature T_c indicated as a function of potassium fraction x in $(NH_4)_{2(1-x)}K_{2x}$-$Pb[Cu(NO_2)_6]$. The solid line is a theoretical curve described in the text.

complex [21]. From the gradient of the log T_1 vs. T^{-1} plot shown in Fig. 3, $E_a = (2 \pm 0.5)$ kJ mol^{-1} was estimated. This agrees very well with the value derived from the foregoing concentration dependence of T_c according to our model. This clearly indicates that the model is reasonable for the present problem. In Fig. 3, ^{1}H T_1 deviates from the linear relationship at higher temperatures. This is probably due to the contribution of the spin-rotation mechanism becoming important as an origin of proton spin-lattice relaxation [22].

The isotope shift of T_c by deuteration can also be consistently explained by the present model. Since the moment of inertia of ND_4^+ is larger than that of NH_4^+, the resident time τ is thought to be longer for the former than the latter [23, 24]. Therefore it is expected from our model that T_c should increase by deuteration because T_c is defined by the temperature, where τ decreases down to a definite value of $(J_{AF}/J_F)\,\tau^*$ with increasing temperature. The observed T_c for $(NH_4)_2Pb[Cu(NO_2)_6]$ increased by ca. 5 K on deuteration in accordance with the above prediction, as shown in Table 1.

In spite of the rather crude approximation employed in our theory, the experimental results could be well interpreted in terms of the theory. This clearly indicates that the motion of the ammonium ions plays an important role for the occurrence of the III–IV phase transition of the present complex.

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[1] T. Asaji, R. Ikeda, and D. Nakamura, Z. Naturforsch. **34b,** 1722 (1979).
[2] B. V. Harrowfield and R. Weber, Phys. Lett. **38A,** 27 (1972).
[3] Y. Noda, M. Mori, and Y. Yamada, J. Phys. Soc. Japan **45,** 954 (1978).
[4] M. Mori, Y. Noda, and Y. Yamada, Solid State Commun. **27,** 735 (1978).
[5] B. V. Harrowfield, A. J. Dempster, T. E. Freeman, and J. R. Pilbrow, J. Phys. C: Solid State Phys. **6,** 2058 (1973).
[6] D. Reinen, C. Friebel, and K. P. Reetz, J. Solid State Chem. **4,** 103 (1972).
[7] C. Friebel, Z. Anorg. Allg. Chem. **417,** 197 (1975).
[8] D. Reinen, Solid State Commun. **21,** 137 (1977).
[9] T. Asaji, L. S. Prabhumirashi, and D. Nakamura, Z. Naturforsch. **41a,** 1154 (1986).
[10] L. S. Prabhumirashi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **85,** 1142 (1981).
[11] Gmelins Handbuch der anorganischen Chemie, **60,** Cu(B), p. 1208, Verlag Chemie, Weinheim 1965.
[12] T. Mukoyama, J. Japanese Chem. **10,** 103 (1956).
[13] H. Flaschka and H. Abdine, Z. Anal. Chem. **144,** 415 (1955).
[14] H. Flaschka, A. M. Amin, and A. Holasek, Z. Anal. Chem. **138,** 241 (1953).
[15] K. Negita, N. Nakamura, and H. Chihara, Chem. Phys. Lett. **63,** 187 (1979).
[16] Y. Yoshioka, N. Nakamura, and H. Chihara, J. Chem. Soc., Faraday Transact. 2, **79,** 497 (1983).
[17] H. Chihara and N. Nakamura, in: Adv. in Nuclear Quadrupole Resonance (J. A. S. Smith, ed.). Heyden, London 1980, Vol. 4, p. 1.
[18] L. G. Olsson, U. Dahlborg, and T. Mänsson, Chem. Phys. Lett. **53,** 413 (1978).
[19] U. Dahlborg, K. E. Larsson, and E. Pirkmajer, Physica **49,** 1 (1970).
[20] Y. Oyanagi and T. Nakagawa, Program Library in Computation Center of Nagoya University, code number 466.
[21] V. B. Nalbandyan, I. N. Belyaev, and G. P. Protsenko, Zh. Neorg. Khim. **24,** 2097 (1979).
[22] R. Ikeda and C. A. McDowell, Chem. Phys. Lett. **14,** 389 (1972).
[23] D. E. Woessner and B. S. Snowden, Jr., J. Phys. Chem. **71,** 952 (1967).
[24] J. S. Waugh and É. I. Fedin, Soviet Phys. Solid State **4,** 1633 (1963).