The Lowest-Temperature Phase Transition of the Mixed Crystal of (NH₄)$_2$(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 (NH₄)$_2$(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 (NH₄)$_2$Cd$_2$(NO$_2$)$_6$. This isotope effect is well interpreted in terms of the above model.

Introduction

Ammonium lead (II) hexanitrocuprate(II), (NH₄)$_2$Pb[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$_2$Pb[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$_2$Pb[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 (NH₄)$_2$(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 (NH₄)$_2$Cd$_2$(NO$_2$)$_6$ having a very similar structure to that of (NH₄)$_2$Pb[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 temperatures 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
Mixed crystals $\text{(NH}_4\text{)}_2\text{(1}_x\text{K}_2\text{)}\text{Pb[Cu(NO}_2\text{)]}_6$ were prepared by a method described in [11]. A mixture of $\text{NH}_4\text{NO}_3$ and $\text{KNO}_3$ was used instead of $\text{NH}_4\text{NO}_3$. $(\text{ND}_4)_2\text{Pb[Cu(NO}_2\text{)]}_6$ was obtained by adding a $\text{D}_2\text{O}$ solution of $\text{ND}_2\text{Cl}$, $\text{Pb(NO}_3\text{)]}_2$, and $\text{CuCl}_2$ to a $\text{D}_2\text{O}$ solution of $\text{NaNO}_2$ in a dry box filled with $\text{N}_2$ gas. The samples prepared were dried in a desiccator over $\text{P}_2\text{O}_5$ and sealed in a glass ampoule for the DTA measurements with a little amount of $\text{He}$ as an exchange gas. $(\text{NH}_4)_2\text{Cd}_2\text{(NO}_2\text{)]}_6$ was synthesized similarly from $\text{NH}_4\text{NO}_3$, $\text{Cd(NO}_3\text{)]}_2$, and $\text{NaNO}_2$.

The potassium fractions in $\text{(NH}_4\text{)}_2\text{(1}_x\text{K}_2\text{)}\text{Pb[Cu(NO}_2\text{)]}_6$ were determined by the so called mercuric chloride method using sodium tetraphenyl-boron as a precipitating reagent [12–14]. For the analysis, the sample was dissolved in a dilute $\text{HNO}_3$ solution in a teflon beaker. Then, a solution of potassium free $\text{NaOH}$ (Merck, $<0.0002$ wt%) was added. The resultant solution was heated nearly to dryness over a water bath to remove $\text{NH}_3$. The residue was dissolved in acetic acid, and the pH of the solution was adjusted to 4.5 by use of $\text{CH}_3\text{COONa}$. Finally, potassium was precipitated as $\text{K[(C}_6\text{H}_5\text{)]}_4\text{B]}$ by adding an $\text{Na[(C}_6\text{H}_5\text{)]}_4\text{B]}$ 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 $\text{(NH}_4\text{)}_2\text{(1}_x\text{K}_2\text{)}\text{Pb[Cu(NO}_2\text{)]}_6$ 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. $T_e(\Pi \rightarrow \Pi)$ and $T_c$ showed a fairly
Table 1. Phase transition temperatures $T_\text{c}(\text{II} \rightarrow \text{I})$, $T_{\text{tr}}(\text{III} \rightarrow \text{II})$, and $T_c$ determined by DTA measurements for $(\text{NH}_4)_2(1-x)\text{K}_x\text{Pb}[\text{Cu(NO}_2\text{)}_6]$ and $(\text{D}_4)_2\text{Pb}[\text{Cu(NO}_2\text{)}_6]$. The mole fraction of potassium determined by chemical analysis is indicated by $x$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$x$</th>
<th>$T_{\text{tr}}(\text{II} \rightarrow \text{I})/K$</th>
<th>$T_{\text{tr}}(\text{III} \rightarrow \text{II})/K$</th>
<th>$T_c/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{ND}_4)_2\text{Pb}[\text{Cu(NO}_2\text{)}_6]$</td>
<td>–</td>
<td>310 ± 1</td>
<td>280 ± 7</td>
<td>99 ± 1</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{Pb}[\text{Cu(NO}_2\text{)}_6]$</td>
<td>–</td>
<td>315 ± 2</td>
<td>286 ± 1</td>
<td>94 ± 1</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2(1-x)\text{K}_x\text{Pb}[\text{Cu(NO}_2\text{)}_6]$</td>
<td>0.046 ± 0.002</td>
<td>314 ± 2</td>
<td>287 ± 1</td>
<td>90 ± 2</td>
</tr>
<tr>
<td>0.096 ± 0.002</td>
<td>312 ± 1</td>
<td>287 ± 1</td>
<td>83 ± 3</td>
<td></td>
</tr>
<tr>
<td>0.099 ± 0.009</td>
<td>312 ± 1</td>
<td>287 ± 1</td>
<td>81 ± 2</td>
<td></td>
</tr>
<tr>
<td>0.169 ± 0.002</td>
<td>311 ± 2</td>
<td>286 ± 1</td>
<td>77 ± 3</td>
<td></td>
</tr>
<tr>
<td>0.187 ± 0.002</td>
<td>308 ± 1</td>
<td>286 ± 1</td>
<td>65 ± 10</td>
<td></td>
</tr>
<tr>
<td>0.204 ± 0.002</td>
<td>308 ± 1</td>
<td>286 ± 1</td>
<td>64 ± 6</td>
<td></td>
</tr>
<tr>
<td>0.216 ± 0.003</td>
<td>308 ± 1</td>
<td>286 ± 1</td>
<td>60 ± 9</td>
<td></td>
</tr>
<tr>
<td>0.228 ± 0.002</td>
<td>307 ± 1</td>
<td>285 ± 1</td>
<td>56 ± 9</td>
<td></td>
</tr>
<tr>
<td>0.276 ± 0.002</td>
<td>304 ± 1</td>
<td>285 ± 1</td>
<td>–</td>
<td></td>
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</tbody>
</table>

Discussion

The angular dependence of the ESR spectra observed for the phases of $(\text{NH}_4)_2\text{Pb}[\text{Cu(NO}_2\text{)}_6]$ 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 $(\text{NH}_4)_2(1-x)\text{K}_x\text{Pb}[\text{Cu(NO}_2\text{)}_6]$ with $x = 0.169$ does not undergo the III $\rightarrow$ 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 $\text{R}_2\text{Pb}[\text{Cu(NO}_2\text{)}_6]$ 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 $\rightarrow$ III phase transition is strongly related to the reorientation of ammonium ions. Since the crystal structure of III is only slightly distorted from the Fm$3$ 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 $(\text{NH}_4)_2\text{Pb}[\text{Cu(NO}_2\text{)}_6]$. Here, we assume that the phase transition III $\rightarrow$ 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 $\tau$ and in a rotational state within a transient time $\tau^*$. 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

$$\tau \equiv \frac{(\tau J_F - \tau^* J_{AF})}{(\tau + \tau^*)}. \quad (1)$$

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

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

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

$$\tau = \frac{J_{AF}}{J_F} \tau^*. \quad (3)$$

For the mixed crystal of $(\text{NH}_4)_{2(1-x)}\text{K}_2\text{Pb}[\text{Cu(NO}_2)_6]$, (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 $\text{NH}_4^+$ is replaced by $\text{K}^+$:

$$\frac{3}{4} \frac{[(1-x)(\tau J_F - \tau^* J_{AF})/(\tau + \tau^*)] - x J_{AF}^*}{x J_{AF}}. \quad (4)$$

Since $J_{AF}^* \approx J_{AF}$, we have at $T_c$

$$\tau = \frac{J_{AF}}{[(1-x)J_F-xJ_{AF}]} \tau^*. \quad (5)$$

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

$$\tau = \tau_x \exp \left( \frac{E_a}{RT} \right), \quad (6)$$

where $E_a$ and $\tau_x$ 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

$$\ln \tau_x + \frac{E_a}{RT} = \ln \tau^* - \ln \left\{ [1-x] J_F/J_{AF} - x \right\}. \quad (7)$$

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

$$\ln \tau_x + \frac{E_a}{RT_c} = \ln \tau^* - \ln \left( J_F/J_{AF} \right). \quad (8)$$

Here, $T_c$ denotes $T_e$ for the pure system. By subtracting (8) from (7), one obtains

$$1 - \frac{T_c}{T_e} = \pi \ln (1 - \beta x), \quad (9)$$

where

$$\pi = \frac{RT_c}{E_a}, \quad \beta = \frac{(J_F+J_{AF})}{J_F}. \quad (10)$$

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 $\alpha$ and $\beta$ as adjustable parameters. Thus $E_a$ and $\beta$ were obtained as $(3 \pm 1)$ kJ mol$^{-1}$ and $(4.0 \pm 0.4)$, 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 $(\text{NH}_4)_2\text{Pb}[\text{Cu(NO}_2)_6]$ because of its paramagnetism. Therefore, the temperature dependence of $^1$H $T_1$ was studied for $(\text{NH}_4)_2\text{Cd}_2[\text{NO}_2]_6$, 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 $(\text{NH}_4)_{2(1-x)}\text{K}_2\text{Pb}[\text{Cu(NO}_2)_6]$. The solid line is a theoretical curve described in the text.](image)
complex [21]. From the gradient of the log $T_1$ vs. $T^{-1}$ plot shown in Fig. 3, $E_a = (2 \pm 0.5) \text{kJ mol}^{-1}$ 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, $^1H T_1$ 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 $\tau$ 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 $\tau$ decreases down to a definite value of $(J_{\text{AF}}/J_F)^\tau$ with increasing temperature. The observed $T_c$ for (NH$_4$)$_2$Pb[Cu(NO$_2$)$_6$]$_{214}$ 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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