

PROTON MAGNETIC RELAXATION IN (NH₄)₂ZnCl₄

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RECENTLY many incommensurate ferroelectrics with a general formula (Me)₂ZnX₄ where Me = NH₄, Rb and X₄ = Cl, Br have attracted attention because of many interesting physical properties¹⁻³. (NH₄)₂ZnCl₄, which belongs to this family, undergoes commensurate-incommensurate phase transition around $T_c = 266^\circ\text{K}$ ⁴ and is reported to be ferroelectric below 194°K . Proton spin-lattice relaxation investigations have been carried out by us in this compound to study the dynamics of NH₄⁺ reorientation and to get possible information about the correlation if any between the phase transition and the motion of the ammonium ion. Proton spin-lattice relaxation times (T_1) have been measured in a polycrystalline sample in the temperature range $77-460^\circ\text{K}$ using a home-made solid state pulsed NMR spectrometer working at 10 MHz⁵.

The temperature dependence of T_1 is shown in Fig. 1. T_1 varies smoothly around the phase transition temperatures $T = 266^\circ\text{K}$ and $T = 194^\circ\text{K}$. It goes through a minimum at 93°K with $T_{1/\text{min}} = 6\text{msec}$. Below this temperature it increases very little with temperature. There seems to be a possibility of a second minimum occurring below 93°K . On the other hand, towards the high temperature side, T_1 goes through a maximum with $T_{1/\text{max}} = 5.42\text{sec}$ around 272°K . At 311°K there is a sudden drop in the value of T_1 by a factor of 2. At 319°K there is a change in the slope of the curve.

There are two dominant relaxation mechanisms in this compound. In the low temperature region intramolecular dipole-dipole interaction between the protons of ammonium ion dictate the relaxation. On the other hand $T_{1/\text{max}}$ at the high temperature suggests that spin-rotation interaction dominates in this region. The temperature at which $T_{1/\text{max}}$ occurs (271°K) and the temperature at which the reported incommensurate phase transition occurs (266°K) are quite close suggesting that the spin rotation interaction of ammonium ions and the incommensurate phase transition are interconnected. T_1 , however, changes smoothly around the reported ferroelectric phase transition temperature ($T_c = 194^\circ\text{K}$), which suggests that the ammonium ions may not have a significant contribution in the ferroelectric phase transition. The sudden drop in the value of T_1 around 311°K could be attributed to a phase transition or a correlation time discontinuity.

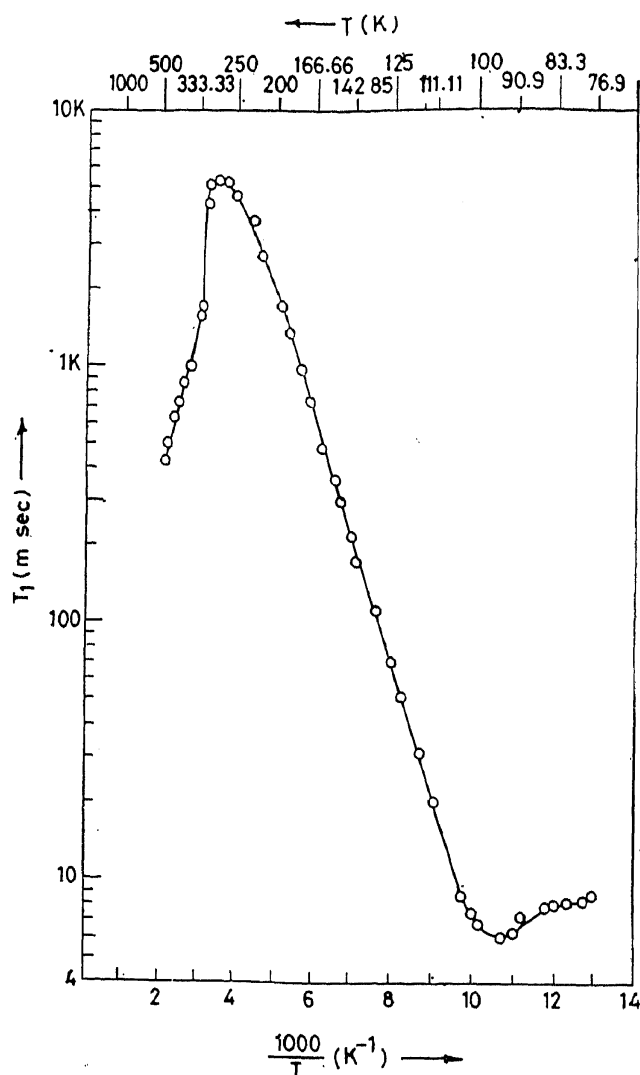


FIG. 1

Using BPP relaxation mechanism, caused by modulation of intramolecular dipole-dipole interaction by random thermal reorientation of the ammonium ions, the activation energy for the potential barrier hindering the motion has been calculated to be 2.2K cal/mol ⁶. Further investigations are in progress and these will be published elsewhere.

October 3, 1981.

1. Sawada, Sh., Shiroishi, Y., Yamamoto, A., Takashige, M. and Matsuo, M., *J. Phys. Soc. Japan*, 1977, **43**, 2089.
2. Moskalev, A. K., Belabrova, I. A. and Aleksandrea, I. P., *Fiz. tverdogo tela*, 1978, **20**, 3288.
3. Sawada, Sh., Shiroishi, Y., Yamamoto, A., Takashige, M. and Matsuo, M., *J. Phys. Soc. Japan*, 1977, **43**, 2101.
4. Belabrova, I. A., Moskalev, A. K., Bizukina N. V., Milul, S. V. and Aleksandrea, I. P. *Solid State Communications*, 1980, **33**, 1101.

5. Shenoy, R. K., Ramakrishna, J. and Jeffrey, K. R., *Pramāna*, 1979, 13, 1.
6. Abragam, A., *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961, p. 457.

HABIT MODIFICATION CAUSED BY 2-THIOURACIL DURING THE ELECTRO-DEPOSITION OF COPPER ON COPPER (100) FACE

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THE mode of action of addition agents in modifying the habit of electrodeposits at the molecular level has been reported¹⁻². Usually the addition agents are found to increase the cathodic overpotential during the deposition process³. In the present report, the effect of 2-thiouracil during the electrodeposition of copper from acid sulphate bath on copper (100) single crystal plane, with respect to both surface topography and electrokinetic parameters has been studied. The notable feature is that this compound causes a reduction in overpotential and brings beneficial changes in the brightness of the deposit.

The copper single crystal was mechanically polished and then electropolished in 1:1 aqueous orthophosphoric acid bath at a constant cell potential of 1.2 V⁴. The electrolytic bath whose purity was controlled⁵ had the composition 0.25 M CuSO₄ · 5H₂O, 0.1 M H₂SO₄ and the required concentration of 2-thiouracil. The deposition was carried out at 2, 5, 10 and 15 mA cm⁻² to a thickness of 3.6 μ at 25 ± 1°C. The overpotential during the deposition process was recorded using an Elico digital pH meter with reference to a freshly prepared copper electrode. The surface appearance after the deposition was examined using a phase contrast microscope at a magnification of 625 ×.

In the case of pure solution at low current densities (2 and 5 mA cm⁻²) a layer type of growth was obtained as noticed by earlier workers⁶. It was observed that the distance between steps in the layer type of deposit decreased, as the concentration of 2-thiouracil was increased from 10⁻¹⁰ to 10⁻⁷ mol l⁻¹. When the concentration of 2-thiouracil was 10⁻⁶ mol l⁻¹, the layer type of deposit was completely transformed into ridge type of deposit. The ridges were perpendicular to the layers. At a concentration of 10⁻⁵ mol l⁻¹, very narrow ridge growth was observed. When the concentration of 2-thiouracil was increased to 10⁻⁵ mol l⁻¹, the deposit became polycrystalline. Further addition of 2-thiouracil made the surface dirty grey and non-uniform.

At higher current densities (10 and 15 mA cm⁻²), in case of pure solution, the deposit consisted of pyramids in the background of layers (Fig. 1). At a concentration of 10⁻¹⁰ mol l⁻¹ of 2-thiouracil, the number of pyramids slightly decreased and layers were observed. When the concentration was increased to 10⁻⁹ mol l⁻¹, truncated pyramids and layers were observed. At a concentration of 10⁻⁸ mol l⁻¹, the pyramidal growths completely disappeared and the distance between the layers became very small. When the concentration of 2-thiouracil was increased to 10⁻⁷ mol l⁻¹, only ridge growth was noticed. At 10⁻⁶ mol l⁻¹, the ridges were still narrow (Fig. 2) and at a concentration of 10⁻⁵ mol l⁻¹, a uniform bright deposit was observed. Further increase in concentration to 10⁻⁴ mol l⁻¹, resulted in a polycrystalline deposit (Fig. 3). If the concentration of 2-thiouracil in the bath was further increased, the deposit became dull grey and non-uniform.

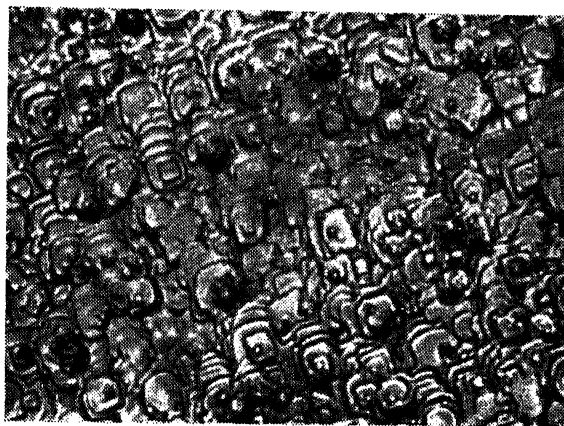


FIG. 1. Pyramids in the background of layers when copper is deposited on copper (100) face from pure solution at 10 mA cm⁻² (magnification 625 ×).

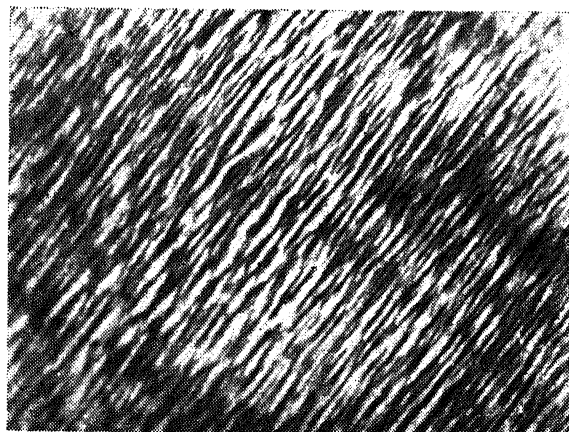


FIG. 2. Narrow ridges when copper is deposited on copper (100) face from acid sulphate bath containing 10⁻⁶ mol l⁻¹ of 2-thiouracil at 10 mA cm⁻² (magnification 625 ×).