

## NATURE OF THE SPONTANEOUS POLARIZATION IN FERROELECTRIC MERCURATES

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Proton resonance in polycrystalline specimens of ferroelectric tetramethylammonium-trihalo-mercurate ( $N(CH_3)_4HgX_3$ , where X is Cl, Br, or I) is studied in the temperature interval in which appreciable change of the rate and character of reorientation of the  $[N(CH_3)_4]^+$  ion is observed. It is found that hydrogen does not play an essential role in the mechanism of spontaneous polarization in these ferroelectrics.

RECENTLY Fatuzzo and Nitsche<sup>[1]</sup> found that crystals of the family  $A(CH_3)_4HgX_3$ , where A is N or P and where X is Cl, Br, or I, are ferroelectric at room temperature. On increase of temperature, none of these reach the Curie point, since the crystals decompose before attainment of the paraelectric range.

The structure of one of the compounds of the family,  $N(CH_3)_4HgBr_3$ , was studied by White<sup>[2]</sup>. The monoclinic crystals of  $N(CH_3)_4HgBr_3$  have lattice parameters  $a = 9.05 \pm 0.02$ ,  $b = 15.90 \pm 0.05$ ,  $c = 7.94 \pm 0.02$  Å, and  $\beta = 93.6 \pm 0.2^\circ$  and contain four molecules in the unit cell. The space group is  $P2(C_2^2)$ .

Among the known crystals in which ferroelectricity is observed, representatives of the family under consideration merit a rather special place: these are the only ferroelectrics that contain mercury; furthermore, only very few ferroelectrics have no oxygen. For these reasons, study of the mechanism of spontaneous polarization in these compounds is of considerable interest.

The presence of hydrogen in the crystals suggests, in a general way, that in the mechanism of spontaneous polarization in these ferroelectrics a significant role may be played by ordering of the hydrogen bonds, as occurs, for example, in potassium dihydrophosphate,  $KH_2PO_4$ <sup>[3]</sup>, lithium hydrazinium sulfate,  $LiN_2H_5SO_4$ <sup>[4]</sup>, and the like.

White, however, on the basis of his structural studies, proposed that in  $N(CH_3)_4HgBr_3$  there is an entirely different mechanism of spontaneous polarization<sup>[2]</sup>. The structural elements of this compound are the  $HgBr_3$  groups, in which the central mercury atom departs insignificantly from the plane of the triangle formed by the three Br atoms. These groups form chains along the C axis, the polar axis of the crystal. Distributed be-

tween these chains are almost regular  $NC_4$  tetrahedra (the position of the hydrogen was not determined in this research).

In White's opinion, the spontaneous polarization in  $N(CH_3)_4HgBr_3$  arises from the fact that the deviation of the bivalent positive mercury atom from the plane of the three bromine atoms produces an appreciable dipole moment of the  $HgBr_3$  group, cumulative for all the four groups of an elementary cell of the crystal. Then a reversal of the direction of the spontaneous polarization under the influence of an applied field of opposite polarity is accomplished by a coherent transition of the  $(HgBr_3)^-$  groups, in which the mercury atom finds itself on the other side of the plane of the three bromine atoms.

Study of ferroelectrics of the  $N(CH_2)_4HgX_3$  type by the method of proton magnetic resonance makes it possible to answer the question, whether hydrogen plays an essential role in the mechanism of spontaneous polarization in these crystals.

In the spectrometer for broad lines, described earlier<sup>[5]</sup>, at temperatures from room temperature to  $-190^\circ C$ , the proton magnetic resonance spectra of polycrystalline  $N(CH_3)_4HgCl_3$ ,  $N(CH_3)_4HgBr_3$ , and  $N(CH_3)_4HgI_3$  were recorded. In addition, the spectrum of  $N(CH_3)_4HgCl_3$  at temperature  $4.3^\circ K$  was, at our request, kindly recorded by Yu. S. Karimov in the Institute of Physics Problems of the USSR Academy of Sciences. Figure 1 shows some of the recorded spectra, and Fig. 2 shows the temperature dependence of the second moment  $S_2$ <sup>[6]</sup> for polycrystalline  $N(CH_3)_4HgCl_3$ .

Theoretical forms of the spectra and values of the second moments for compounds that contain methyl groups  $CH_3$ , "at rest" or reorienting themselves about various axes, are given in the

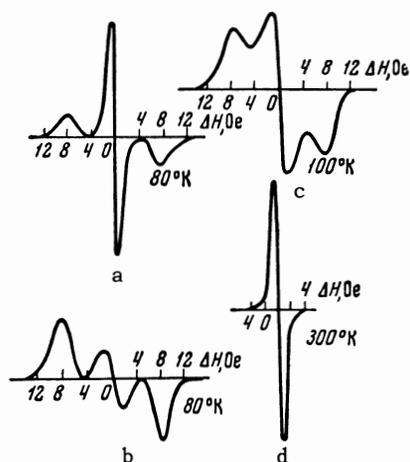


FIG. 1. Proton magnetic resonance spectra of polycrystalline specimens at the temperatures indicated on the figure: a,  $N(CH_3)_4HgI_3$ ; b, c, and d,  $N(CH_3)_4HgCl_3$ .

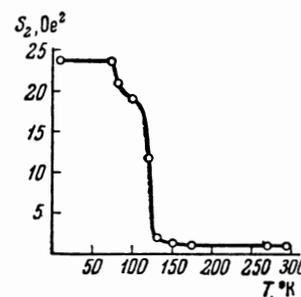
papers of Powles and Gutowsky<sup>[7]</sup>. Also presented there is a great amount of experimental data on proton resonance in compounds that contain such groups.

Comparison of the form of the spectra obtained by us experimentally, and of the values of the second moments calculated from them, with the corresponding experimental values shows that at temperature  $-190^\circ C$  the methyl groups in  $N(CH_3)_4HgCl_3$  are fixed "rigidly".

However, upon increase of temperature by only a few degrees, the reorientation frequency<sup>[6]</sup> of the methyl groups about the C-N bonds reaches an appreciable value ( $\sim 10^4$  cps), and this leads to a diminution of the value of  $S_2$ . On further increase of temperature, the size of  $S_2$  decreases sharply to a value of about  $1 \text{ Oe}^2$  at temperatures above  $150^\circ K$ . Such a small value of the second moment at these temperatures is evidence that here there is occurring an energetic reorientation of the whole  $[N(CH_3)_4]^+$  ion about random axes.

The experimental data obtained for  $N(CH_3)_4HgBr_3$  and  $N(CH_3)_4HgI_3$  show that the temperature at which a diminution of the size of the second moment begins in these compounds is lowered by a few degrees upon systematic transition from compounds containing Cl to compounds with Br and I; and that, correspondingly, the potential barrier for reorientation of the

FIG. 2. Temperature dependence of the second moment for polycrystalline  $N(CH_3)_4HgCl_3$ .



$[N(CH_3)_4]^+$  ion, highest for  $N(CH_3)_4HgCl$ , gradually decreases for compounds with Br and I.

All three of the compounds studied remain ferroelectric over a wide temperature interval, in which there occurs an appreciable change of the mobility of the  $[N(CH_3)_4]^+$  ion: at some temperatures it is "at rest", at others it reorients itself energetically about random axes. This fact is evidence that hydrogen bonds cannot play an essential role in the mechanism of spontaneous polarization in these ferroelectrics. In this sense the results obtained do not contradict the paper of White, mentioned above, which attributes the presence of spontaneous polarization in  $N(CH_3)_4HgBr_3$  to the presence of a large dipole moment of the  $HgBr_3$  group.

<sup>1</sup> E. Fatuzzo and R. Nitsche, *Phys. Rev.* **117**, 936 (1960); E. Fatuzzo, R. Nitsche, H. Roetschi, and S. Zingg, *Phys. Rev.* **125**, 514 (1962).

<sup>2</sup> J. G. White, *Acta Cryst.* **16**, 397 (1963).

<sup>3</sup> W. Känzig, *Ferroelectrics and Antiferroelectrics*, in *Solid State Physics*, Vol. 4, pp. 1-197, Academic Press, New York, 1957 (Russ. Transl., IIL, 1960).

<sup>4</sup> J. D. Cuthbert and H. E. Petch, *Can. J. Phys.* **41**, 1629 (1963).

<sup>5</sup> A. G. Lundin and G. M. Mikhaïlov, *PTÉ* **2**, 90 (1960).

<sup>6</sup> E. R. Andrew, *Nuclear Magnetic Resonance*, Cambridge Univ. Press, 1955 (Russ. Transl., IIL, 1957).

<sup>7</sup> J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.* **21**, 1695 (1953); **21**, 1704 (1953); **23**, 1692 (1955).

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