

phys. stat. sol. (b) 53, K99 (1972)

Subject classification: 14.4.1 and 19

L.V. Kirenskii Institute of Physics,

Siberian Department of the Academy of Sciences of USSR, Krasnoyarsk

On the Nature of the Temperature Dependence of NMR Spectra Second Moment  
in Order-Disorder Type Ferroelectrics

By

N.A. SERGEEV and YU.G. KUBAREV

The application of the NMR method for the investigation of ferroelectric crystals gives valuable information about the position and dynamics of the ferroelectric dipoles, which permits to understand the microscopic mechanism of the ferroelectric phase transition in many cases (1). In turn the NMR method in ferroelectrics has some peculiarities, which demand a deeper understanding of some aspects of the present NMR theory. One of these peculiarities is for example the behaviour of the spin-lattice relaxation time ( $T_1$ ) at the Curie point  $T_c$  and in its neighbourhood. The use of quasi-spin wave model gives a simple interpretation of apparent anomaly of  $T_1$  (2 to 5). Another peculiarity of NMR in ferroelectrics is the subject of our consideration. There are changes of NMR spectrum second moment ( $S_2$ ) near  $T_c$  in some (5, 6) ferroelectrics. For the explanation of the change of the second moment  $S_2$  many author use the formula of Bloembergen, Purcell, and Pound (BPP) (7, 8), modified by Gutowsky and Pake (9)

$$S_2 = (S_2^I - S_2^{II}) \frac{2}{\pi} \arctg \left( \alpha \frac{\delta\nu}{\nu_c} \right) + S_2^{II}, \quad (1)$$

where  $S_2^{II}$  is the second moment for  $\delta\nu/\nu_c \ll 1$  and  $S_2^I$  for  $\delta\nu/\nu_c \gg 1$ . It should be noted that this formula applied to crystals with mobile molecular groups suggest that the temperature dependence of  $S_2$  is determined only by the temperature dependence of the correlation frequency  $\nu_c$ . However, the changes of the character of molecular group mobility at the phase transition in ferroelectrics are determined by quite other reasons.

In order-disorder type ferroelectric crystals the dipoles are situated in double-minimum potential wells. In the paraelectric phase the dipoles are situated in both minimum with equal probabilities. The change of the mobility of molecular groups and the ferroelectric dipoles connected with them at the transition from paraelectric

to ferroelectric phase is connected with their localization in one potential minimum. As a result the lifetime of the ferroelectric dipoles in the potential minima suffers a jump, whereas the correlation frequency may not change essentially, which is confirmed by recent experimental data on the temperature dependence of  $\nu_c$  near  $T_c$  (5). Therefore, the  $S_2$  change in the vicinity of  $T_c$  may not be connected with a sharp decrease of  $\nu_c$  and there is a certain interest in determining of reasons which lead to the apparent behaviour of  $S_2$ .

Let us consider as an example a ferroelectric with two spin groups which are situated in a double-minimum potential well, which, of course, does not limit the common character of the present consideration.

The NMR spectrum second moment of such a crystal is determined by the spectral density  $J^{(o)}(\nu)$  of the autocorrelation function  $G(t) = \langle F^{(o)}(t) F^{(o)}(0) \rangle$ , where  $F^{(o)} = r^{-3}(3 \cos^2 \theta - 1)$ ,  $r$  is the distance between two spins,  $\theta$  is the angle between the direction of external magnetic field  $\vec{H}$  and vector  $\vec{r}$ . It may be expressed by (8, 10)

$$S_2 = W \int_{-\alpha \delta \nu}^{\alpha \delta \nu} J^{(o)}(\nu) d\nu + \beta^2,$$

where  $W = \frac{3}{4} \gamma^4 \hbar^2 I(I+1)$ ,  $\beta$  is the intermolecular contribution to  $S_2$  which we shall neglect in the further consideration,  $\delta \nu \approx S_2^{1/2}$  is the halfwidth of NMR spectrum, and the parameter  $\alpha$  is introduced because of the uncertainty of the integration limits. The autocorrelation function in our case is equal to (1)

$$G(t) = \frac{a}{(1+a)^2} (F_1 - F_2)^2 e^{-t/\tau_c} e^{\left(\frac{aF_1 + F_2}{1+a}\right)^2},$$

where  $F_1$  and  $F_2$  are the values of  $F^{(o)}$  in the first (1) and second (2) minimum of the potential well;  $a = W_{21}/W_{12}$ ;  $1/\tau_c = W_{21} + W_{12}$ ;  $W_{21}$  is the transition probability of the ferroelectric dipole from the second minimum to the first one,  $W_{12}$  is the probability of the reverse transition.

Then we get

$$S_2 = W \frac{a}{(1+a)^2} (F_1 - F_2)^2 \frac{2}{\pi} \arctg \left( \alpha \frac{\delta \nu}{\nu_c} \right) + W \left( \frac{aF_1 + F_2}{1+a} \right)^2. \quad (2)$$

This expression agrees with the BPP formula (1) (7, 9) where

$$S_2' = W \left[ \frac{a}{1+a} F_1^2 + \frac{1}{1+a} F_2^2 \right] , \quad S_2'' = W \left[ \frac{a}{1+a} F_1 + \frac{1}{1+a} F_2 \right]^2 .$$

One can see from (2) that the apparent change of  $S_2$  may be explained by the change of the transition probabilities between the potential minima (i.e.  $a$ ), but not by change of correlation frequency  $\nu_c$ . Indeed, when  $\nu_c$  does not change essentially at the transition from the paraelectric to the ferroelectric phase, i.e.  $\nu_c \approx 10^{11}$  to  $10^{12}$  Hz (5) in all temperature range considered, we have

$$S_2 = W \left( \frac{a F_1}{1+a} + \frac{F_2}{1+a} \right)^2 . \quad (3)$$

Expression (3) reflects the common method of local field averaging in the presence of the molecular group mobility for  $\delta\nu/\nu_c \ll 1$  (11, 12).

The values  $a/1+a$  and  $1/1+a$  are the probabilities of ferroelectric dipoles being in the first and in the second potential minimum and they are connected simply with their average reduced dipole moment  $p$  (2):

$$\frac{a}{1+a} = \frac{1}{2} (1+p) , \quad \frac{1}{1+a} = \frac{1}{2} (1-p) .$$

Thus

$$S_2 = W \left[ \frac{F_1 + F_2}{2} + \frac{p(F_1 - F_2)}{2} \right]^2 .$$

In the paraelectric phase  $p = 0$  and

$$S_2 = W \left( \frac{F_1 + F_2}{2} \right)^2 .$$

In the ferroelectric phase  $p = 1$  and

$$S_2 = W F_1^2 .$$

Hence the temperature dependence of the NMR spectrum second moment near  $T_c$  is determined by the temperature dependence of the polarization and therefore the study of the anomalous behaviour of  $S_2$  in the vicinity of  $T_c$  gives valuable information about both the position of ferroelectric dipoles in the crystal lattice and their dynamics during the transition from the paraelectric to the ferroelectric phase per-

mitting the determination of the transition type.

In conclusion it should be emphasized that the mechanism mentioned above takes place probably at the change of the NMR spectra second moment at another phase transition different from the ferroelectric phase transitions.

The authors are indebted to Prof. A.G. Lundin, O.V. Falaleev, and Yu.N. Moskvich for helpful discussions.

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(Received August 2, 1972)