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ON SOME POSSIBILITIES OF DETERMINING THE VOLUME OF KÀNZIG REGIONS IN FERROELECTRICS

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Abstract. — Several methods for determining the volume of Kanzig Regions in ferroelectrics from different experimental data (thermal, electrical, dynamic of crystal, etc.) are considered. Theoretical aspects of different cooperative phenomena are discussed.

Diffuse ferroelectric phase transitions (D. F. P. T.) are regarded at present as a rather common phenomenon. Since there is no general molecular theory of the phase transitions so far, their nature has to be explained on the basis of some phenomenological model. The most elaborated in this respect is the Model of Kanzig Regions (M. K. R.) [1], [2] according to which a ferroelectric near its phase transition point is assumed to be comprised of a number of so called Kanzig Regions (K. R.). Such regions have been first observed experimentally by W. Kanzig [3], and to the present time there is a number of considerations suggesting that the K. R. behave like equilibrated thermodynamical systems. A direct confirmation to these conclusions recently has been provided by G. Shirane and collaborators [4] having observed quasi-elastic scattering of slow neutrons on polarization seeds which the authors [4] refer to as critical fluctuations.

The volume of the K. R. is one of the parameters determining the degree and the nature of D. F. P. T. For this reason the estimation of the volume of K. R. is of doubtless interest. The linear dimensions of the K. R. first were determined from X-ray data by Kanzig and appeared to be $10^{-5}$–$10^{-6}$ cm [3]. All of the existing methods for estimating the volume of the K. R. at present are based essentially on a number of principles which can be conditionally classified into several groups as follows hereafter.

1° Different models according to which the calculated or measured experimentally quantities depend on the volume $v_k$ of an individual K. R. as a physical parameter. In this case experimentally measured values of the corresponding physical quantities may be used to determine the volume $v_k$. The anomalous heat capacity $C_a(T)$ is considered as a particular example of this kind. According to the M. K. R. three methods may be offered to determine the $v_k$ [5], [6], [7]. The first exists in calculating the $v_k$ from maximum value of the anomalous capacity $C_{a_{\text{max}}}$:

$$v_k = \frac{4 k T_k^2 C_{a_{\text{max}}}}{Q_0^2},$$

where $k$ is the Boltzman factor $T_k$-the Curie temperature, $Q_0$-transition heat. The other method is related to the half-width $\tau$ of the curve $C_s(T)$:

$$v_k = \frac{1.76 k T_k^2}{\tau Q_0} = \frac{2.43 \times 10^{-16} T_k^2}{\tau Q_0}.$$  (2)

The third method of estimating the $v_k$ is based on finding the switching function $n/N(T)$ from the anomalous heat capacity. It gives:

$$v_k(T) = \frac{k T_k^2}{Q_0} \ln \left[ \frac{N}{n} (T) - 1 \right];$$  (3)

where $\Delta T = T_k - T$. This method, in distinction to the first two, enables to obtain the $v_k$ as a function of temperature $v_k = v_k(T)$.

The calculations of $v_k$ by means of formulae (1), (2) and (3) on the basis of experimental data for BaTiO$_3$ and solid solution (Ba$_{1-x}$, Sr$_x$)TiO$_3$ are presented in tables I and II correspondingly.

In a similar way the value of $v_k$ can be estimated

<table>
<thead>
<tr>
<th>Table I</th>
<th>Experimental data source</th>
<th>$v_k \times 10^{19}$ ccm according to expression</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>Blattner, Merz [8]</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Volger [9]</td>
<td>14.6</td>
<td>17.3</td>
</tr>
<tr>
<td>Shirane, Takeda [10]</td>
<td>3.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Kanzig, Maikoff [11]</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Borman, Strukov, Taraskin, Fritzberg [12]</td>
<td>13.3</td>
<td>11.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table II</th>
<th>Concentration $x$ in solid solution (Ba$_{1-x}$, Sr$_x$)TiO$_3$ [12]</th>
<th>$v_k \times 10^{19}$ ccm according to expression</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>$x = 0$</td>
<td></td>
<td>13.3</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td></td>
<td>4.1</td>
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<td>1.9</td>
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<tr>
<td>$x = 0.3$</td>
<td></td>
<td>0.9</td>
</tr>
</tbody>
</table>

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from experimental data on some other physical characteristics of ferroelectrics. The basic results are given in table III.

As it is seen from the calculations most of experimental data yield the value of \( v_k \approx 10^{-19}-10^{-18} \text{ccm} \).

**Table III**

<table>
<thead>
<tr>
<th>Physical phenomona</th>
<th>( V_k \times 10^9 \text{ccm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Ray scattering</td>
<td>10-10^4</td>
</tr>
<tr>
<td>Polarization</td>
<td>2-10</td>
</tr>
<tr>
<td>Dielectric permeability</td>
<td>1-90</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>0,9-17</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>2-10</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>1-10</td>
</tr>
<tr>
<td>Polarization switching and hysteresis</td>
<td>1,9-19</td>
</tr>
</tbody>
</table>

2° If the K. R. is considered as a seed of a new phase, the theory of heterophase fluctuations can be applied. In this case the volume of K. R., as a rule, is determined by relation between the bulk and surface energies of the seed. The accuracy of calculations of \( v_k \) by these methods is determined by the accuracy of the surface and bulk energies of the particular ferroelectric material. As a rule, the major difficulties arising here are related to the surface energy which can be found in an indirect way only and has a rather wide dispersion of values. If the conventional values of energy are used, the volume of the seeds (K. R.) is find to be of the order \( 10^{-19}-10^{-18} \text{ccm} \) [20], [21], [27].

3° The estimation of the size of K. R. can be made on the basis of some considerations of the dynamic theory of crystal lattice, e. g. from amplitudes of ion oscillations and areas of coherent rearrangement [28], [29], [30], [31]. This approach yields

\[ v_k \approx 10^{-19}-10^{-17} \text{ccm} \]

A farther progress in these methods is likely to be expected with some ideas of W. Cochran, R. Cowley, N. Bogolubov and others.

These experimental observations thus suggest that in the case of ferroelectric phase transition of a fundamental importance are the K. R. the origin of which is likely to be related to the display of cooperative phenomena. From this point of view the different appearances of these phenomena and the names found in different sources (fluctuations, critical fluctuations, heterophase fluctuations, K. R., areas of coherent rearrangement, correlation radius, etc.) can be assumed to have essentially a common basis.

It should be noticed that a more detail study of the part played by cooperative phenomena in ferroelectric phase transitions requires proper experiments to be performed. Especially it concerns the effects of different conditions (pressure, composition, etc.).

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[30] IVIN (V. A.) and ROLOV (B. N.), in Diffuse Phase Transitions, issue 4, Latv. State University, Riga, 1972, p. 4, 19.