Letters to the Editor

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An Extension of the Theory of Mason and Matthias to the Low Temperature Transitions in $BaTiO_3$

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THE notation of the original paper by Mason and Matthias[1] is here followed except that β_x, β_y, β_z are used to denote the Lorentz factors for the x, y, z crystallographic directions, and P_x, P_y, P_z always refer to permanent polarizations.

Mason and Matthias use the Boltzmann principle to derive the expression (Eq. (17) of their paper)

$$P_z=\frac{N\mu\sinh[(E_z+\beta_zP_z/1-\beta_z\gamma)\mu/kT]}{2+\cosh[(E_z+\beta_zP_z/1-\beta_z\gamma)\mu/kT]}$$

leading to the conclusion that for $E_z=0$ solutions other than $P_z=0$ can occur only if the function $A_z=[(\beta_zN\mu^2/1-\beta_z\gamma)1/kT]\geqslant 3$ giving the "Curie" temperature T_c.

They further derive a similar expression for P_y in the presence of the resulting spontaneous P_z (Eq. (40)) but go on to suggest after replacing the hyperbolic sine by its argument and the hyperbolic cosine by unity (Eq. (71) but replacing E_y by E_z) that no non-zero solutions are possible in the absence of an external field. However, if we consider the more exact Eq. (40) and put $E_y=0$ we obtain

$$P_y=\frac{N\mu\sinh[(\beta_yP_y/1-\beta_y\gamma)\mu/kT]}{1+\cosh[(\beta_zP_z/1-\beta_z\gamma)\mu/kT]+\cosh[(\beta_yP_y/1-\beta_y\gamma)\mu/kT]}. \quad (1)$$

We may write

$$A_y=\left[\left(\frac{\beta_yN\mu^2}{1-\beta_y\gamma}\right)\frac{1}{kT}\right],\quad A_z=\left[\left(\frac{\beta_zN\mu^2}{1-\beta_z\gamma}\right)\frac{1}{kT}\right]\quad\text{as above.}$$

$$\therefore\ \frac{P_y}{N\mu}=\frac{\sinh(A_yP_y/N\mu)}{1+\cosh(A_zP_z/N\mu)+\cosh(A_yP_y/N\mu)}\simeq\frac{\sinh(A_yP_y/N\mu)}{3\cdot6+\cosh(A_yP_y/N\mu)},$$

since

$$\cosh(A_zP_z/N\mu)\simeq2\cdot6. \quad (2)$$

Hence solutions for $P_y\neq0$ can occur if $A_y\geqslant4$.

If we assume that $\beta_y=0.123$, we find that the critical temperature for the occurrence of a further spontaneous polarization P_y when P_z already exists is $T_2\simeq275$°K.

We shall here assume that the system takes on the form given by the symmetrical solution $P_y=P_z$ and $A_y=A_z\geqslant4$ as this is in accord with recent x-ray determinations of the symmetry of single crystals.[2] This implies an initial drop in P_z to about $\frac{3}{4}$ of its former value in order that Eq. (2) may remain unchanged. We have further

$$P_x=\frac{N\mu\sinh[(\beta_xP_x/1-\beta_x\gamma)\mu/kT]}{\cosh[(\beta_zP_z/1-\beta_z\gamma)\mu/kT]+\cosh[(\beta_yP_y/1-\beta_y\gamma)\mu/kT]+\cosh[(\beta_xP_x/1-\beta_x\gamma)\mu/kT]}.$$

Assuming that the mean value of β varies in accordance with Mason and Matthias, Fig. 11, that $A_y=A_z=4.1$ and that $P_y=P_z$ remains $\frac{3}{4}$ of the room temperature value we obtain

$$\frac{P_x}{N\mu}=\frac{\sinh(A_xP_x/N\mu)}{6\cdot4+\cosh(A_xP_x/N\mu)},\quad\text{where}\quad A_x=[(\beta_xN\mu^2/1-\beta_x\gamma)1/kT].$$

Hence there are solutions for $P_x\neq0$ if $A_x\geqslant4.8$, so that $T_3\simeq180$°K giving the critical temperature for occurrence of P_x. However, if we determine the critical temperature for three equal mutually perpendicular polarizations from the equation.

$$P_x=\frac{N\mu\sinh[(\beta_xP_x/1-\beta_x\gamma)\mu/kT]}{3\cosh[(\beta_xP_x/1-\beta_x\gamma)\mu/kT]},$$

we find $T_3'\simeq150$°K using the same β-curve. This determines the temperature of break up of the rhombohedral form when heated from lower temperatures and would be expected to be greater than that calculated for the same transition on cooling and it therefore seems likely that the average value of β falls off slightly less rapidly as the temperature is lowered than Mason and Matthias indicate. A value of $\beta\simeq0.11$ at 180°K gives agreement between the two values of $T_3\simeq(180$°K).

The above solutions are the symmetrical ones and would presumably be the stable ones for an infinite single domain crystal but in any real crystal twinning and boundary effects will result in slight variations of the local field in different domains and even within a domain and this may well result in stability of slightly asymmetric solutions (i.e., $P_y=P_z+\delta P$, etc.) which would account for the diffuseness observed in x-ray reflections at low temperatures, particularly from polycrystalline specimens. This is confirmed by very accurate parameter measurements on "single" crystals in the region +18°C–40°C by the present author where it is found that the variations in spacing are essentially confined to the y–z plane of the above notation. These measurements will be published in detail subsequently.

It may be noted here that the theory depends essentially only on the existence of a dipole array having the assumed symmetry properties, the question as to whether this is the result of a titanium or oxygen ion shift or other charge displacement (e.g., covalent bonds) being irrelevant. The exact treatment when two or more polarizations occur together requires the solution of simultaneous equations; nevertheless the above simplified theory gives very satisfactory agreement with experiment.

[1] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948).
[2] Kay, Vousden, and Wellard, Nature **163**, 636 (1949).

A Note on Plasma Oscillation

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IT is interesting to note that some of the plasma oscillation effects recently described in papers by Bohm and Gross[1,2] have been observed in vacuum tubes and were explained by a similar analysis.[3] Particularly, oscillations sometimes occur in the electron beams of traveling-wave tubes because of the presence of positive ions. The oscillations have discrete frequencies in the range of the estimated plasma frequencies of the ion clouds.

These oscillations were described in terms of an equation, (16) of reference 3, which is the one dimensional form of (7) of reference 1. An expansion similar to that of (10) of reference 1 was used in connection with the velocity distribution. While the effect of ion velocity on the rate of increase of the wave was considered, collisions were not taken into account in the analysis.

A case of a finite beam filling a tube and confined by a magnetic field was also analyzed. In such a case, the electron beam can excite not only plasma oscillations of the ions, but oscillations of ions in the magnetic field as well. These oscillations would usually have a lower frequency than plasma oscillations, and they were suggested as an explanation for lower frequency fluctuations which had been observed.

[1] D. Bohm and E. P. Gross, Phys. Rev. **75**, 1851 (1949).
[2] D. Bohm and E. P. Gross, Phys. Rev. **75**, 1864 (1949).
[3] J. R. Pierce, J. App. Phys. **19**, 231 (1948).