

with Eq. (4). Using $g_{\text{eff}} = 2.05$ and $\mu = 2.2$ Eq. (4) gives a value of $x = 0.24$ which is quite reasonable. It is important that further measurements be made at higher frequencies on the nickel ferrite aluminates to obtain data on the frequency dependence of g_{eff} .

At the composition near $t = 0.7$ the shift in g_{eff} from high to low values is tentatively identified with the assumption that the magnetic moment on the A sites becomes greater than the contribution of the B sites. The interpretation given by Eq. (2) is that the change in g_{eff} is a consequence of the algebraic sum of the spins and magnetic moments going through zero at slightly different compositions. This simple picture lends validity to the foregoing assumption that the magnetic moment on the A sites is the dominant one for $t > 0.7$. When the samples are quenched, the rearrangement of the ions in a more random condition shifts the moment back to the B sites with a corresponding large change in g values. It is of course necessary that the g values be different for the two ions, in this case Ni^{++} and Fe^{+++} , or for the same ion in different sites, otherwise the change in distribution of the various magnetic atoms

either due to heat treatment or chemical composition would not alter the ratio which gives g_{eff} .

CONCLUSIONS

It is seen from this work that there can be large variations in the resonance behavior of a substitutional ferrite and that for any particular composition further changes can be effected depending on the particular heat treatment the specimen has undergone. With the aid of Eq. (2) a simple interpretation of both very large and small g values is possible, and this in turn bears on the broader question of the exact distribution of ions for the specimen.

ACKNOWLEDGMENTS

I wish to thank both Dr. R. K. Wangsness and Dr. J. S. Smart for many helpful discussions of this work, and Dr. L. R. Maxwell for his advice on experimental problems which have arisen. I am indebted to Mr. E. P. Wenzel for his cooperation in the recording of the resonance curves.

Effect of a Two-Dimensional Pressure on the Curie Point of Barium Titanate*

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By hydraulic means, a single crystal of barium titanate in the shape of a flat circular disk was subjected to a pressure exerted on its edges and not on its faces. A very slight pressure removed all domains that were not normal to the disk. The stress system then consisted of equal pressures on the two a axes, and no pressure on the c axis. The transition temperature increased with the square of the two-dimensional pressure, while, according to Merz, a hydrostatic pressure produces a linear drop. Using Devonshire's expansion for the free energy and the appropriate Legendre transformation, the free energy, depending on polarization and pressure, was obtained for both two-dimensional and hydrostatic stress systems. This yielded a purely linear-pressure dependence, and it was, therefore, necessary to supplement Devonshire's expansion with higher terms in order to obtain a quadratic effect.

Although it was too difficult to evaluate the effect of pressure

on the transition temperature itself when higher terms were included, it was easy to determine the effect on the Curie-Weiss temperature T_0 . This is the temperature at which the inverse susceptibility of the cubic phase extrapolates to zero, and its pressure dependence will be the subject of a future paper. For both two-dimensional and hydrostatic pressures, the linear part of the shift of the Curie-Weiss temperature was found to depend only on the lower terms in the free energy, and provide two independent relations for determining the two g coefficients. The quadratic shift of the Curie-Weiss temperature depends on the higher terms with which Devonshire's expansion was supplemented, and a reasonable interpretation of these higher terms gave an upward direction to the quadratic shift of the Curie-Weiss temperature.

INTRODUCTION

IT has long been known that substitution of strontium for barium in barium titanate^{1,2} causes a drop in the Curie temperature that depends linearly on the strontium concentration. This has been explained as the

result of an effective decrease of the unit-cell size caused by the smaller strontium ions. If, instead, the unit-cell size is reduced by application of hydrostatic pressure, the transition temperature decreases with decreasing unit-cell size at about the same rate.³ The substitution of lead for barium, on the other hand, raises the transition temperature at a rate depending linearly on the lead concentration.² Lead titanate itself has a much higher Curie temperature (490°C) and is much more

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¹ A. von Hippel *et al.*, National Defense Research Council Reports 14-300, 1944 and 14-540, 1945 (unpublished); von Hippel, Breckenridge, Chesley, and Tisza, *Ind. Eng. Chem.* **38**, 1097 (1946).

² D. F. Rushman and M. A. Strivens, *Trans. Faraday Soc.* **A42**, 231 (1946).

³ W. J. Merz, *Phys. Rev.* **78**, 52 (1950).

strongly tetragonal.⁴ In fact, optical observations on crystals grown in the laboratory⁵ show that it remains tetragonal all the way down to liquid helium temperatures, although with a rapid drop of the birefringence. The effect of hydrostatic pressure has been discussed by Slater⁶ in terms of his statistical model of barium titanate. In this model, the local potential seen by the Ti ion, that is, the potential exclusive of dipole interaction, is represented by *one* harmonic potential well of cubic symmetry, supplemented by a small, fourth-power term to keep the spontaneous polarization finite. If the lattice size is reduced by hydrostatic compression (or strontium substitution), the oxygen ions that surround the Ti ion tetrahedrally are pressed more tightly against the Ti ion. The consequent stiffening of the local harmonic potential well requires a greater local field caused by dipole interaction to displace the Ti ion a given distance.

A two-dimensional pressure, however, should have quite a different effect, for the crystal will contract along two axes but expand along the third. If the two axes undergoing compression are cubic axes, the local potential well will acquire tetragonal symmetry and will become football shaped, or possibly even dumbbell shaped. The latter would mean that the single local potential well has become a double well, which would result in an order-disorder type of transition if the barrier between the two wells were comparable to kT . The way in which a two-dimensional pressure affects the Curie transition in barium titanate will depend very critically on how the z expansion is related to the x contraction, and particularly on how the internal field is affected by these strains. One may say that the change in the local potential well produced by a two-dimensional pressure should allow the Ti ion to displace more freely in the z direction. On the other hand, an expansion of the lattice in the polarization direction and contractions across the polarization direction should reduce the local field.

APPLICATION OF TWO-DIMENSIONAL PRESSURES

Bridgman⁷ has made studies of plastic flow and fracture of a number of substances under two-dimensional compression. One method was to use a specially constructed steel die that could actually push on a ductile material in two directions at once, and the other method was to exert a pull in one direction on a sample subjected to hydrostatic pressure. The latter method amounts to a two-dimensional pressure superposed on a hydrostatic compression that is less than the applied hydrostatic pressure by the strength of the pull. In the

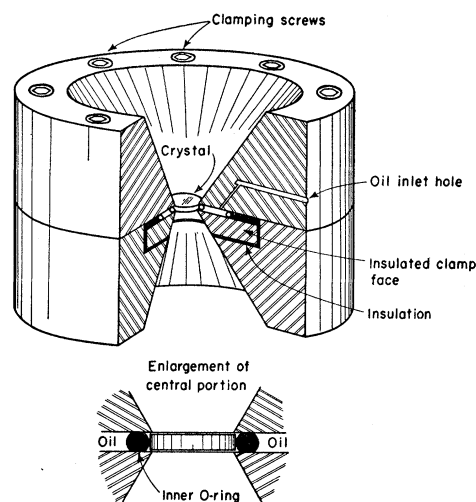


FIG. 1. Details of crystal holder for applying two-dimensional pressure.

present work, we have developed a method of exerting a uniform two-dimensional compression on the edges of a disk-shaped sample with pressures up to, and probably well above, 1000 atmospheres. While this is small compared to the range of two-dimensional pressure obtainable by Bridgman's second method, our technique has the advantage of leaving the faces of the disk exposed, so that one can make optical and x-ray measurements and apply electric fields.

The method relies on a rubber "O-ring," which is a circular ring of soft rubber with a circular cross section. The O-ring is placed around the disk-shaped sample and the combination is clamped in a steel clamp as shown in Fig. 1. The faces of the clamp have openings to permit direct observation of the crystal. The clamp is tightened, thereby flattening the O-ring, until the separation of the faces of the clamp is only *ca* 2 mils greater than the thickness of the crystal. This clearance allows free expansion of the crystal in the direction not subjected to pressure. Oil is forced into the clamp as shown in the figure by means of a hydraulic pump. The pressure of the oil pushes the O-ring against the edges of the crystal, and the O-ring prevents the oil from leaking out. The outside seal is accomplished by another O-ring. The clamp used in the present work was designed so that one face of the clamp is electrically insulated, although the electrical measurements have not yet been made. Observation with a microscope was sufficient to determine the transition temperature. By introducing quartz windows, it will be possible to apply a different pressure to the faces of the crystal, and to study the effect of a superposition of hydrostatic pressure on a two-dimensional pressure. Since a soft rubber has a low shear modulus, sticking of the rubber to the faces of the clamp should not create a large pressure correction at the pressure used. However, if the O-ring is lubricated before clamping, the rubber can

⁴ Shirane, Hoshino, and Suzuki, *Phys. Rev.* **80**, 1105 (1950); G. Shirane and E. Sawaguchi, *Phys. Rev.* **81**, 458 (1951).

⁵ H. H. Rogers, Technical Report 56, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1952 (unpublished).

⁶ J. C. Slater, *Phys. Rev.* **78**, 748 (1950).

⁷ P. W. Bridgman, *Large Plastic Flow and Fracture* (McGraw-Hill Book Company, Inc., New York, 1952).

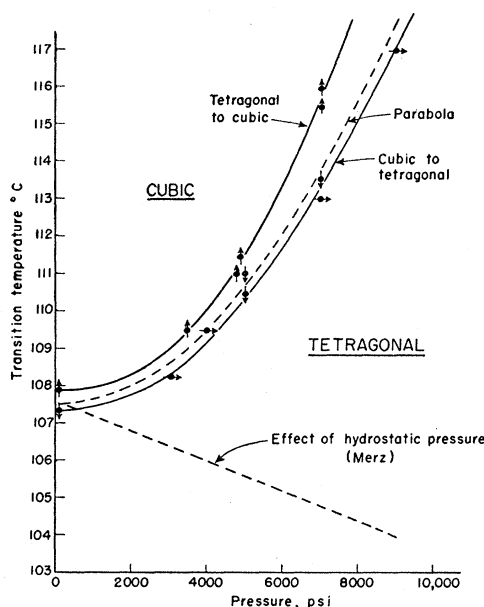


FIG. 2. Effect of two-dimensional pressure on the Curie transition in barium titanate.

relax back and forth between the faces of the clamp fairly rapidly under changes in pressure. The data can be taken in such a manner as to allow a check on the presence or absence of a frictional correction in the pressure, which is read by means of a Bourdon gauge in the oil line.

EFFECT ON TRANSITION TEMPERATURE

The disk-shaped crystal was cut from a strain-free crystal plate of cubic-growth habit and of uniform thickness. Its diameter was a little over $\frac{1}{8}$ in. and its thickness, *ca* 20 mils. The thickness to diameter ratio of about 1:8 should be sufficient to prevent elastic buckling. The clamp was wound with nichrome ribbon and well insulated with glass cloth. Temperatures were measured by means of a mercury thermometer embedded deeply in the massive metal of the clamp. The transition was observed with a polarizing microscope, which revealed a considerable disturbance at the transition point. The transition was reasonably sharp at all pressures. The effect of pressure on the transition was followed by zigzagging isothermally and isobarically along the transition curve. The agreement of the down-going transition temperatures taken isothermally and isobarically shows that the rubber transmitted the pressure without appreciable frictional correction (Fig. 2). Unfortunately, the upgoing transition could be taken only isobarically due to the insensitive needle valve in the hydraulic pump. The results show a purely quadratic dependence of the transition temperature on two-dimensional pressure. The width of thermal hysteresis increases with two-dimensional pressure. The results of Merz,³ using hydrostatic pressure, show a purely linear pressure dependence. If, for convenience,

the two-dimensional and hydrostatic pressure effects are symbolized by $2-H$ and $3-H$, respectively, the results can be described as follows, where H is the oil pressure in atmospheres and T_c the transition temperature:

$$2-H: \quad T_c = T_{c0} + 3.1 \times 10^{-5} H^2,$$

$$3-H \text{ (Merz)}^3: \quad T_c = T_{c0} - 0.0058 H.$$

EFFECT OF PRESSURE ON DEVONSHIRE'S FREE-ENERGY EXPANSION

Devonshire⁸ has expressed the free energy of barium titanate in terms of polarization and strain, with respect to the cubic unpolarized configuration, as

$$\begin{aligned} A(\mathbf{x}, \mathbf{P}) = & \frac{1}{2} c_{11}^P (x_x^2 + y_y^2 + z_z^2) + c_{12}^P (y_y z_z + z_z x_x + x_x y_y) \\ & + \frac{1}{2} c_{44}^P (x_y^2 + y_z^2 + z_x^2) + \frac{1}{2} \chi'' (P_x^2 + P_y^2 + P_z^2) \\ & + \frac{1}{4} \xi_{11}'' (P_x^4 + P_y^4 + P_z^4) \\ & + \frac{1}{2} \xi_{12}'' (P_y^2 P_z^2 + P_z^2 P_x^2 + P_x^2 P_y^2) \\ & + g_{11} (x_x P_x^2 + y_y P_y^2 + z_z P_z^2) \\ & + g_{12} \{ x_x (P_y^2 + P_z^2) + y_y (P_z^2 + P_x^2) \\ & + z_z (P_x^2 + P_y^2) \} + g_{44} (y_z P_y P_z + z_x P_z P_x \\ & + x_y P_x P_y) + \frac{1}{6} \chi'' (P_x^6 + P_y^6 + P_z^6). \quad (1) \end{aligned}$$

The boldface symbols mean the stress or strain tensors and the vector polarization, the components of all of which are in the above expression. For the present purposes, we need not consider configurations involving shears or any components of polarization aside from that in the z direction. We are thus considering the dependence of the free energy on x_x, y_y, z_z, P_z (which we shall abbreviate x, y, z, P), all other strain components (the shears) and the x and y components of polarization being kept equal to zero:

$$\begin{aligned} A(\mathbf{x}, \mathbf{P}) = & \frac{1}{2} c_{11}^P (x^2 + y^2 + z^2) + c_{12}^P (yz + zx + xy) \\ & + \frac{1}{2} \chi'' P^2 + \frac{1}{4} \xi_{11}'' P^4 + g_{11} z P^2 \\ & + g_{12} (x + y) P^2 + \frac{1}{6} \chi'' P^6. \quad (2) \end{aligned}$$

Using the convention that a positive stress shall be a compression and a positive strain an extension, we find that the three stress components are $X = -\partial A / \partial x$, $Y = -\partial A / \partial y$, $Z = -\partial A / \partial z$, and thus for a two-dimensional pressure:

$$\begin{aligned} -H &= c_{11} x + c_{12} (y + z) + g_{12} P^2, \\ -H &= c_{11} y + c_{12} (z + x) + g_{12} P^2, \\ 0 &= c_{11} z + c_{12} (x + y) + g_{11} P^2, \end{aligned} \quad (3)$$

where the superscripts P of the elastic coefficients at constant polarization have been dropped for convenience. For a hydrostatic pressure, the stress equations (3) are the same except that the zero in the third line is replaced by $-H$.

To discuss the Curie point and the properties asso-

⁸ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949); **42**, 1065 (1951).

ciated with the z direction, we need only compare cubic and tetragonal configurations, so that the strains x and y are equal, and the stress relations become

$$3-H: \begin{cases} -H = \\ -H = \end{cases}, \quad 2-H: \begin{cases} -H = (c_{11}+c_{12})x + c_{12}z + g_{12}P^2, \\ 0 = 2c_{12}x + c_{11}z + g_{11}P^2, \end{cases} \quad (4)$$

which can be solved for x and z , giving

$$\begin{aligned} 2-H: \quad x &= -\frac{c_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \\ &\quad -\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}P^2, \\ z &= \frac{2c_{12}}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \\ &\quad +\frac{2c_{12}g_{12}-(c_{11}+c_{12})g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}P^2; \\ 3-H: \quad x &= -\frac{(c_{11}-c_{12})}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \\ &\quad -\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}P^2, \\ z &= -\frac{(c_{11}-c_{12})}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \\ &\quad +\frac{2c_{12}g_{12}-(c_{11}+c_{12})g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}P^2. \end{aligned} \quad (5)$$

If we now substitute these expressions for the strains into the free energy [Eq. (2)], remembering that $x=y$, we obtain for both cases

$$A(\mathbf{x}, \mathbf{P}) = \text{terms in } H^2 + \text{terms in } HP^2 + \text{terms in } P^2 \\ + \text{terms in } P^4 + \text{terms in } P^6. \quad (6)$$

We can now determine the free energy $A(\mathbf{X}, \mathbf{P})$ expressed in terms of stress and polarization, and see how it compares with the free energy as a function of polarization at zero stress,⁸ for which the most recent coefficients have been given by Merz.⁹ The free energy in terms of stress and polarization is related to that in terms of strain and polarization by the usual Legendre transformation:¹⁰

$$A(\mathbf{X}, \mathbf{P}) = A(\mathbf{x}, \mathbf{P}) + \mathbf{x} \cdot \mathbf{X}, \quad (7)$$

where $\mathbf{x} \cdot \mathbf{X}$ is a scalar product, and is the transformation term that must be added to Eq. (6) to obtain the free energy expressed in terms of polarization and pressure.

⁹ W. J. Merz, Phys. Rev. **91**, 513 (1953).

¹⁰ See, for instance, L. Tisza, *Phase Transformations in Solids* (John Wiley and Sons, Inc., New York 1951), pp. 1-38.

The transformation term is

$$\mathbf{x} \cdot \mathbf{X}_{2-H} = 2Hx = a \text{ term in } H^2$$

$$-2\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}HP^2, \quad (8)$$

$$\mathbf{x} \cdot \mathbf{X}_{3-H} = 2Hx + Hz = a \text{ term in } H^2$$

$$-2\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}HP^2 \\ +\frac{2c_{12}g_{12}-(c_{11}+c_{12})g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}HP^2.$$

Therefore,

$$A(\mathbf{X}, \mathbf{P}) = \text{terms in } H^2 + \text{terms in } HP^2 + A_P, \quad (9)$$

where A_P is the free energy as a function of polarization for zero stress, the coefficients of which have recently been given by Merz as

$$A_P = 3.7 \times 10^{-5}(T - T_0)P^2 - 1.7 \times 10^{-13}P^4 + 3.8 \times 10^{-23}P^6.$$

T_0 is the Curie-Weiss temperature at atmospheric pressure and is about 11°C below the transition temperature, and the units are electrostatic cgs units.

The only terms through which the pressure can affect the dependence of the free energy on the polarization are terms containing both H and P , in this case [Eq. (9)], the terms in HP^2 . If these terms add up to a positive quantity, pressure will raise the free energy of the polarized configurations faster than that of the unpolarized phase, and so lower the transition temperature; if they add up to a negative quantity, it is raised.

Having found the transformation terms [Eq. (8)], we now need to calculate the contribution of $A(\mathbf{x}, \mathbf{P})$ to terms containing both H and P . The terms in $A(\mathbf{x}, \mathbf{P})$ that give terms in H and P (*viz.*, HP^2) are as follows, where we have set $x=y$ since we are only interested in comparing cubic and tetragonal configurations:

$$(c_{11}+c_{12})x^2 + \frac{1}{2}c_{11}z^2 + 2c_{12}xz + g_{11}zP^2 + 2g_{12}xP^2.$$

For a two-dimensional pressure the sum of the terms in HP^2 in $A(\mathbf{x}, \mathbf{P})$ is

$$\begin{aligned} &\{ (c_{11}+c_{12})2[c_{11}(c_{11}g_{12}-c_{12}g_{11})] \\ &\quad + (\frac{1}{2}c_{11})2[2c_{12}(2c_{12}g_{12}-(c_{11}+c_{12})g_{11})] \\ &\quad + 2c_{12}[-2c_{12}(c_{11}g_{12}-c_{12}g_{11})] + 2c_{12}[-c_{11}(2c_{12}g_{12} \\ &\quad - (c_{11}+c_{12})g_{11})] \} HP^2 / (c_{11}-c_{12})^2 (c_{11}+2c_{12})^2 \\ &\quad + (g_{11}2c_{12}-2g_{12}c_{11})HP^2 / (c_{11}-c_{12})(c_{11}+2c_{12}). \end{aligned}$$

The second and fourth terms within the braces cancel, and the first and third terms, when added together and factored, become $2(c_{11}g_{12}-c_{12}g_{11})(c_{11}-c_{12})(c_{11}+2c_{12})$, which, when multiplied by the quantity outside braces, exactly cancels the last term in the whole expression, which means that for a two-dimensional pressure, $A(\mathbf{x}, \mathbf{P})$ contributes no terms in HP^2 .

However, for hydrostatic pressure the free energy $A(\mathbf{x}, \mathbf{P})$ contributes $-2c_{12}g_{11}/(c_{11}-c_{12})(c_{11}+2c_{12})HP^2$. Therefore, when we add on the transformation terms [Eq. (8)], the HP^2 term in $A(\mathbf{X}, \mathbf{P})$ is

$$\frac{-2g_{12}(c_{11}-c_{12})-g_{11}(c_{11}+c_{12})}{(c_{11}-c_{12})(c_{11}+2c_{12})}HP^2 \text{ for 3-}H$$

and

$$-2\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}HP^2 \text{ for 2-}H.$$

The free energy in terms of polarization and pressure is then

$$\begin{aligned} 2-H: A(\mathbf{X}, \mathbf{P}) = A_c + & \left[3.7 \times 10^{-5}(T - T_0) \right. \\ & \left. - 2\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \right] P^2 \\ & - 1.7 \times 10^{-13}P^4 + 3.8 \times 10^{-23}P^6, \end{aligned} \quad (12)$$

$$\begin{aligned} 3-H: A(\mathbf{X}, \mathbf{P}) = A_c + & \left[3.7 \times 10^{-5}(T - T_0) \right. \\ & \left. - \frac{2(c_{11}-c_{12})g_{12} + (c_{11}+c_{12})g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \right] P^2 \\ & - 1.7 \times 10^{-13}P^4 + 3.8 \times 10^{-23}P^6. \end{aligned}$$

From this it is seen that the dependence of free energy on polarization, for a given applied pressure, is unaltered only if there is a corresponding change in temperature ΔT :

$$\begin{aligned} 2-H: \Delta T = & \frac{1}{3.7 \times 10^{-5}} \left[2\frac{c_{11}g_{12}-c_{12}g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \right], \\ 3-H: \Delta T = & \frac{1}{3.7 \times 10^{-5}} \left[\frac{2(c_{11}-c_{12})g_{12} + (c_{11}+c_{12})g_{11}}{(c_{11}-c_{12})(c_{11}+2c_{12})}H \right]. \end{aligned} \quad (13)$$

Since a purely linear dependence of the transition temperature on two-dimensional pressure is thus predicted, it is necessary to supplement Devonshire's expansion with higher terms in order to account for the quadratic effect. While it is too difficult to evaluate the effect of pressure on the transition temperature itself in the presence of the higher terms, it will be shown that the effect on the Curie-Weiss temperature T_0 is easy to determine. This may be determined experimentally by extrapolating to zero the inverse susceptibility of the cubic phase. Its dependence upon two-dimensional and hydrostatic pressure will be the subject of a future paper. It will be shown in the following section that the linear part of the shift in the Curie-Weiss temperature for two-dimensional and hydrostatic pressures gives two independent linear relations connecting the coefficients g_{11} and g_{12} , and the quadratic

shifts give two linear relations connecting the 9 coefficients in the higher terms with which Devonshire's expansion may be supplemented.

EFFECT OF HIGHER TERMS IN THE FREE ENERGY ON THE CURIE-WEISS TEMPERATURE

As a result of the symmetry of the crystal, the strains with respect to the cubic phase depend on even powers of the polarization. Since there is a P^2 term in the strain, the P^6 term in the free energy as a function of stress and polarization [given by Eq. (10) for zero stress] will be partially made up of terms not included in Devonshire's expansion Eq. (1). These are terms in strain $\times P^4$, strain² $\times P^2$, and strain³. For the present case of no shears and no polarization other than P_z , the free energy including these higher terms will be

$$\begin{aligned} A(\mathbf{x}, \mathbf{P}) = & \frac{1}{2}c_{11}P(x^2+y^2+z^2) + c_{12}P(yz+zx+xy) \\ & + \frac{1}{2}\chi''P^2 + \frac{1}{4}\xi_{11}''P^4 + g_{11}zP^2 + g_{12}(x+y)P^2 \\ & + \frac{1}{6}\xi''P^6 + \beta_{11}zP^4 + \beta_{12}(x+y)P^4 \\ & + \gamma_{11}z^2P^2 + \gamma_{12}(x^2+y^2)P^2 + \gamma_{13}xyP^2 \\ & + \gamma_{14}(yz+zx)P^2 + \delta_{11}(x^3+y^3+z^3) + \delta_{12}xyz \\ & + \delta_{13}[y(z^2+x^2)+z(x^2+y^2)+x(y^2+z^2)]. \end{aligned} \quad (14)$$

There is not enough accurate information to evaluate any of these higher terms, but it is easy to show that the terms with coefficients γ and δ give rise to a quadratic dependence of the Curie-Weiss temperature T_0 on the pressure.

The isotherms of polarization *vs* electric field, that Merz⁹ calculates from the free energy, are reproduced in Fig. 3, where t is proportional to $(T - T_0)$, T_0 being the Curie-Weiss temperature. It is easy to show that the transition temperature occurs at the point $t=0.75$ and in Fig. 4 the free energies corresponding to $t=0$, $t=0.75$ and $t=1$ are shown schematically. The Curie-Weiss temperature $t=0$, is clearly the temperature to which the cubic phase could be supercooled in the absence of thermal fluctuations, and the tetragonal phase could be overheated to $t=1$ in the absence of thermal fluctuations. The Curie-Weiss temperature $t=0$ is determined by the condition $(\partial P / \partial E) = \infty$ taken

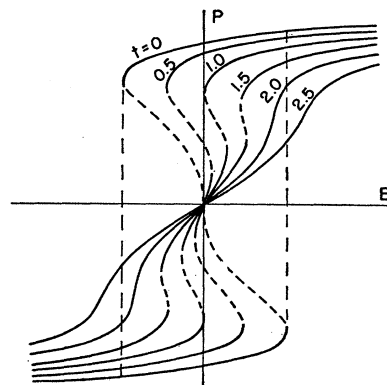
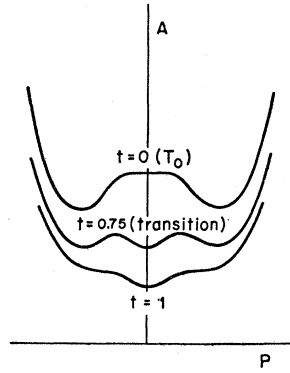


FIG. 3. Merz's isotherms of the electric field.

FIG. 4. Schematic representation of free-energy isotherms in vicinity of transition.



at zero polarization, where the strain polarization relations will be those for very small values of these variables and will, therefore, be given by Eqs. (5), which may be written

$$x = C_1 H + G_{12} P^2, \quad z = C_2 H + G_{11} P^2. \quad (5)$$

When the above strains are substituted into Eq. (14) and the Legendre transformation terms included, the terms in the free energy as a function of polarization and pressure $A(\mathbf{X}, \mathbf{P})$ that contain P^2 and hence determine the slope $\partial P / \partial E$ at $P=0$ and the Curie-Weiss temperature, will be

$$\begin{aligned} \frac{1}{2} \chi'' P^2 + & \left\{ [2(c_{11} + c_{12})C_1 G_{12} + c_{11} C_2 G_{11} \right. \\ & + 2c_{12}(C_1 G_{11} + C_2 G_{12}) + g_{11} C_2 + 2g_{12} C_1] \\ & + \frac{2G_{12}}{2G_{12} + G_{11}} \text{ (for } 2H) \\ & \left. + \frac{2G_{12} + G_{11}}{2G_{12} + G_{11}} \text{ (for } 3H) \right\} H P^2 + [\gamma_{11} C_2^2 + 2\gamma_{14} C_1 C_2 \\ & + (2\gamma_{12} + \gamma_{13}) C_1^2 + 3(2\delta_{11} + 2\delta_{13}) C_1^2 G_{12} \\ & + 3\delta_{11} C_2^2 G_{11} + (\delta_{12} + 2\delta_{13})(C_1^2 G_{11} + 2C_1 C_2 G_{12}) \\ & + 2\delta_{13}(2C_1 C_2 G_{11} + C_2^2 G_{12})] H^2 P^2. \quad (15) \end{aligned}$$

Thus the linear dependence of the Curie-Weiss temperature depends entirely on the coefficients g (and, of course, c , which are known) and is given by Eqs. (13). The quadratic dependence is determined by the coefficients γ and δ , and depends, of course, also on the g and c coefficients.¹¹

For two-dimensional pressure, the linear part of the pressure shift [Eqs. (13)] is seen to be proportional

¹¹ As has been pointed out by Tisza (reference 10), the validity of thermodynamics in the vicinity of a point such as ($t=0$, $P=0$) in Fig. 4 is questionable, since the statistical fluctuations about one of the macroscopic variables will be large. The expression (15), when divided by $P^2/2$, is the inverse susceptibility of the cubic phase as a function of temperature and pressure. As prescribed by Devonshire, the temperature dependence arises only from the coefficient $\chi'' = \chi_0(T - T_0)$, which is a straight line passing through zero at the temperature T_0 . Equation (15) states that the application of pressure shifts the straight line up or down. What we call the shift in the Curie-Weiss temperature, ΔT_0 , is simply the amount of the shift of this straight line in the direction of the temperature axis. The fact that the validity of thermodynamics is questionable when one is very close to the crossing point, does not enter the picture.

to the coefficient G_{12} . If one can assume that the Curie-Weiss temperature changes in more or less the same way as the transition temperature, which has yet to be checked, one would conclude that G_{12} is zero, and, therefore, that the x strain has no P^2 dependence at all. In Fig. 5 are plotted the strains from the x-ray data of Kay and Vousden¹² against the fourth power of the polarization, as recently measured by Merz;⁹ within 25°C of the transition temperature the x strain is directly proportional to P^4 rather than P^2 . One may object to using the results of Kay and Vousden on crystals that gave much too low values for the spontaneous polarization. But Merz has shown that the reason for these low values in crystals that are not exceedingly good is that some tendency to antiparallel domain formation persists to fairly appreciable fields. The x-ray parameters, however, are not affected by the existence of domains. The crystals of Merz have a somewhat lower transition temperature than those of Kay and Vousden, so the data were plotted for corresponding temperatures below the transition temperature.

The nature of the terms with coefficients γ and δ is immediately apparent upon differentiation of the free energy [Eq. (14)]:

$$\begin{aligned} -\partial Z / \partial z &= c_{11} P + 2\gamma_{11} P^2 + 3\delta_{11} z + 2\delta_{13}(x + y), \\ -\partial X / \partial x &= c_{11} P + 2\gamma_{12} P^2 + 3\delta_{11} x + 2\delta_{13}(y + z), \quad (16) \\ -\partial X / \partial y &= c_{12} P + \gamma_{13} P^2 + \delta_{12} z + 2\delta_{13}(x + y), \\ -\partial Z / \partial x &= c_{12} P + \gamma_{14} P^2 + \delta_{12} y + 2\delta_{13}(y + z). \end{aligned}$$

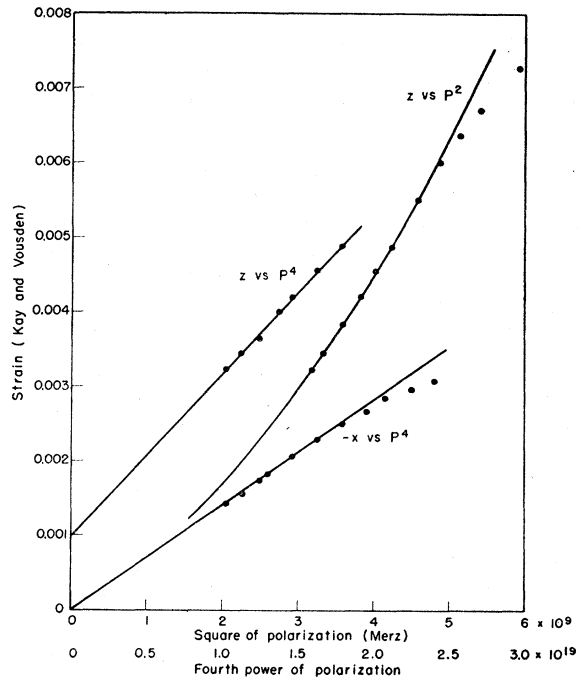


FIG. 5. Plots of the tetragonal strains against powers of the polarization.

¹² H. F. Kay and P. Vousden, *Phil. Mag.* **40**, 1019 (1949).

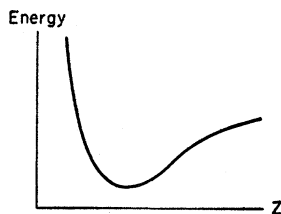


FIG. 6. Typical dependence of energy on an inter-atomic distance.

For the small polarization and strains involved in the present discussion, one can make some qualitative statements about the γ and δ coefficients. Considering the first of the above equations, it states that the mechanical stiffness in the z direction departs from Hooke's law by the quantity $3\delta_{11}z$ when the x and y directions are clamped and the polarization is not allowed to change (since the partial derivatives are taken at constant x, y, P in the first line). This is to be expected, since, with x, y , and P clamped, the energy as a function of extension in the z direction is not a parabola, but is rather as shown in Fig. 6, which to a second approximation has a negative z^3 term in addition to the z^2 term. Hence the coefficient δ_{11} must be a negative quantity. For small changes in the clamped dimensions x and y , the shape of the energy curve in the z direction will probably not change much except to be shifted, so one would expect δ_{13} to be rather small. If one increases the fixed value of the polarization, z will be increased since $z = G_{11}P^2$, and thus γ_{11} must have the same sign as δ_{11} , i.e., negative.

Considering the second of Eqs. (16), the polarization P^2 does not change the strain x for small values, since this depends on P^4 , and, therefore, the coefficient γ_{12} is zero. For the same reason γ_{13} in the third equation is also zero. In the third equation, a small change in the clamped dimension z will not much affect the X, y stress-strain relation, so δ_{12} is small. In the fourth equation, where y and z are clamped, the stress Z produced by a strain x will not be influenced by P since x does not produce any P^2 , and the coefficient γ_{14} is small.

According to the foregoing, one might assume, for qualitative purposes, that the only important coefficients are γ_{11} and δ_{11} . The terms in H^2P^2 in expression (15) then reduce, since G_{12} is zero, to $[\gamma_{11}C_2^2 + 3\delta_{11}C_2^2G_{11}]H^2P^2$ which is a negative quantity, since G_{11} is positive and γ_{11} and δ_{11} are both negative. This means that the quadratic shift of the Curie-Weiss temperature for two-dimensional pressure is upward, as observed. Using Mason's¹³ values $c_{11}P = 2.07 \times 10^{12}$ and $c_{12}P = 1.40 \times 10^{12}$, the value of C_2^2 for the two-dimensional pressure is about 18 times that for hydrostatic pressure, so that

¹³ Bond, Mason, and McSkimin, Phys. Rev. **82**, 442 (1951).

the quadratic effect for hydrostatic pressure is very much smaller, also as observed.

Finally, we may consider the linear dependence of the Curie-Weiss temperature on hydrostatic pressure. If the linear effect for two-dimensional pressure is absent, then $c_{11}g_{12} - c_{12}g_{11} = 0$ from which $g_{12} = 0.68g_{11}$. In order to match the dependence of the Curie-Weiss temperature on hydrostatic pressure to Merz's³ measurement of the transition, it is necessary to assume $g_{11} = -0.17$. Assuming $z = aP^2 + bP^4$, one can match the z strain in Fig. 5 quite accurately within 25°C of the transition by assuming $a = 0.57 \times 10^{-12}$, which requires a value for g_{11} of -1.2 . However, the curve in Fig. 5 suggests negative P^6 or P^8 terms in the strains, and, in fact, the z strain can be accurately represented by $z = 2 \times 10^{-13}P^2 + 3.4 \times 10^{-22}P^4 - 2.9 \times 10^{-32}P^6$, where the coefficient of P^2 requires a value of $g_{11} = -0.42$. This gives a linear dependence on hydrostatic pressure about twice that observed.

PROBABLE EFFECT ON THE HYSTERESIS LOOP

If the shift remains quadratic to much higher pressures, a two-dimensional pressure of 2000 atmos should raise the transition by more than 100°C. This should result in a marked increase of the coercive field at room temperature. Furthermore, it is possible that at room temperature the hysteresis loop is affected by the proximity of the orthorhombic transition around 5°C, since the direction of the polarization might well reverse by a rotation through the orthorhombic configurations rather than by direct passage through the cubic configuration. In this case, the effect of the two-dimensional pressure on the orthorhombic transition would enter into the picture. It is expected that the two-dimensional pressure, as presently applied to two of the pseudo-cubic axes, will cause a very large depression of the orthorhombic transition. The reason for expecting this is that the elongation that accompanies the spontaneous polarization would be working in part against a component of compression, when the polarization direction snaps into a new direction at 45° to the direction in which there is no component of stress. The rhombohedral phase would likewise be suppressed by the two-dimensional pressure as applied at present. From the magnitudes of the effects of two-dimensional and of hydrostatic³ pressures on the orthorhombic transition, it will be possible to obtain information about the shear terms in Devonshire's expansion.

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