BEHAVIOUR OF SPECIFIC HEAT C_p, THERMAL EXPANSION β AND ISOTHERMAL COMPRESSIBILITY k_T NEAR FERROELECTRIC TRANSITIONS

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Abstract

The ordinary concepts of the order of phase changes are not suitable near dielectric transitions which show logarithmic or other infinities in specific heats. The application of the more general Pippard scheme under such circumstances is studied. The linear correlations among the heat capacity, thermal expansion, elastic compressibility and pressure derivative of T_c are discussed in the case of triglycine sulphate, sodium nitrite, potassium-dihydrogen phosphate, barium titanate and lead titanate. In the case of the first two, a discussion of the behaviour of individual coefficients of linear expansion and compliance moduli is also possible. It is suggested that irrespective of the order of the transitions, the Pippard relations should be used whenever the thermodynamic quantities show very large variations as T_c is approached.

Introduction

With the recent studies on λ-transition in liquid helium-4[1], it has been realised that the Ehrenfest's relations for the second-order phase transition break down in the instances where the specific heat C_p, thermal expansion $\beta\,[= v^{-1}(\partial v/\partial T)_P]$ and isothermal compressibility $k_T\,[= -v^{-1}(\partial v/\partial P)_T]$ show logarithmic or other singularities at the transition temperature. A consideration of equilibrium among the phases along S and V curves in a second-order transition leads[2] to the Ehrenfest relations

$$\frac{DP}{DT} = \frac{1}{Tv}\,\frac{C_{p1}-C_{p2}}{\beta_1-\beta_2} = \frac{\beta_1-\beta_2}{k_{T1}-k_{T2}} \qquad [1]$$

where DT/DP is the slope of the equilibrium curve, *i.e.*, change in transition temperature with pressure. With the approach of C_p, β and k_T to infinity according a logarithmic or other power law singularity, the quotient in the Ehrenfest relations becomes indeterminate. Further, in view of the approach of the thermodynamic parameters to infinity from either side of the transition even the concept of discontinuity implied in the Ehrenfest relations becomes questionable[3, 4].

In the case of λ-transition in He^4, this difficulty was overcome by Pippard's idea[5, 6] of cylindrical entropy surface near the transition temperature, which leads to simple expressions among the C_p, β and k_T of any one of the phases near the transition. A close study of this problem shows that in Pippard's scheme the order of transition is quite immaterial and hence without making any further reference to the order of transition or the type of power law singularity, one can use Pippard's scheme for correlating C_p, β and k_T. A critical investigation on the extension of these ideas to the case of ferromagnetic/antiferromagnetic to paramagnetic transitions has been previously reported[4]. In the present study the available thermodynamic data of ferroelectric substances are correlated using the Pippard scheme.

Pippard's Relations near Phase Transitions: In deriving the relations among the thermodynamic quantities in the vicinity of transition temperatures, different, though equivalent, methods have been employed. Originally Pippard[5,6] introduced the assumption that the entropy function close to a λ – transition has a cylindrical shape on account of the very large values of the specific heat. This assumption regarding the shape of the entropy surface leads to two equations,

$$C_p = Tv\left(\frac{DP}{DT}\right)\beta + \text{Constant} \qquad [2]$$

$$\beta = \left(\frac{DP}{DT}\right)k_T + \text{Constant} \qquad [3]$$

Both these equations have been verified at the λ – transitions in liquid helium[1], ammonium chloride, quartz[2] and a number of ferromagnetic and antiferromagnetic transitions[3,4].

An approach more suitable for the present purpose is that of Buckingham and Fairbank[1], who used identities of the type

$$\left.\frac{\partial}{\partial x}\right|_y = \left.\frac{\partial}{\partial x}\right|_z - \left.\frac{\partial}{\partial y}\right|_x \left.\frac{\partial y}{\partial x}\right|_z$$

(where x, y are thermodynamic variables and z a constraint) to obtain exact relations among the thermodynamic quantities. For instance the identity

$$-\left.\frac{\partial v}{\partial T}\right|_p = \left.\frac{\partial S}{\partial p}\right|_T = \left.\frac{\partial S}{\partial p}\right|_\lambda - \left.\frac{\partial S}{\partial T}\right|_p \left.\frac{\partial T}{\partial p}\right|_\lambda$$

can be recast as

$$C_p = Tv\beta\left(\frac{DP}{DT}\right)_\lambda + C_0, \quad \text{where } C_0 = T\left(\frac{DS}{DT}\right)_\lambda \qquad [4]$$

while the identity

$$\left.\frac{\partial v}{\partial p}\right|_T = \left.\frac{\partial v}{\partial p}\right|_\lambda - \left.\frac{\partial v}{\partial T}\right|_p \left.\frac{\partial T}{\partial p}\right|_\lambda$$

can be recast as

$$\beta = k_T \left(\frac{DP}{DT}\right)_\lambda + \beta_0, \text{ where } \beta_0 = v^{-1}\left(\frac{Dv}{DT}\right)_\lambda \qquad [5]$$

The transition occurs at slightly different temperatures when the substance is subjected to different pressure. So quantities like $(DS/DT)_\lambda$ and $(Dv/DT)_\lambda$ are to some extent dependent on p and T. But the variation is so very weak compared to the very large variations of C_p, β and k_T near λ – transitions that $(DS/DT)_\lambda$ and $(Dv/DT)_\lambda$ may be considered "constants" by comparison. This is equivalent to the cylindrical approximation and equations [4], [5] go over to equations [2], [3], where the notation $(DP/DT)_\lambda$ is used for the derivative along the λ line.

It is first noted that for a proper second order phase transition equations [2] and [3] give the Ehrenfest relations [1] between the two phases. If C_p, β and k_T assume very large values near the phase transitions, estimation of quantities like $C_{p1} - C_{p2}$, $\beta_1 - \beta_2$, $k_{T1} - k_{T2}$ is difficult and the ratios in equations [1] become indeterminate, whereas the Pippard relations are still useful. In this case even the order of transition does not matter. Equations [2] and [3] involve quantities pertaining to a single phase and so uncertainties in the entropy or volume changes across the transition (whether finite as in "first order" changes or zero as in "second order" changes) do not affect the correlation among the thermodynamic quantities. Such utility of the Pippard's relations has been emphasized by Renard and Garland[7].

In the last few years Tisza[8], Viswanathan[9], Garland[10] and Janovec[11] have considered extensions of Pippard's relations to crystalline media, where the transition temperature may vary with the components X_i of the stress tensor. It is found [9, 10] that if α_i are the coefficients of thermal expansion and S^T_{ij} the isothermal elastic compliance coefficients,

$$\alpha_i = \gamma_i\, C_p/Tv + \text{Constant} \qquad [6]$$

$$S^T_{ij} = \gamma_j\, \alpha_i + \text{Constant.} \qquad [7]$$

where $\gamma_i = -(DT/DX_i)_\lambda$. In the case of hydrostatic pressures one has

$$\sum_{i=1}^{3} \alpha_i = \beta \; ; \; \sum_{i,j=1}^{3} S^T_{ij} = k_T$$

and so Pippard's relations 2, 3 are obtained with

$$DT/DP = \sum_{i=1}^{3} \gamma_i \qquad [8]$$

Garland[10] has checked equations 6 and 7 in quartz finding that the plots of S_{11} and S_{12} against α_1 and of S_{13} against α_3 have the same slope γ_1. Janovec[11] has considered the application of these relations as well as similar relations for piezoelectric constants to ferroelectric triglycine sulphate. (There are one or two small slips of sign in Janovec's paper which are easily corrected). In particular Janovec has considered the relations

$$S_{ij}^{T} = \gamma_i \gamma_j \left(C_p/Tv\right) + \text{Constant} \qquad [9]$$

obtained from equations 6 and 7. In the present note these equations will be applied to a number of other ferroelectric crystals.

The merit of Pippard's approach lies in its wide range of applicability. Since, as already pointed out, linear correlations among C_p, β and k_T become possible irrespective of the "order of transition", Pippard scheme is particularly useful in the cases for which the order of transition involved is uncertain because of the very large values attained by C_p and β near the transition. The asymptotic value of the slope of C_p versus β or β versus k_T plot gives the true value of DT/DP and so the thermodynamic data should be correlated with sufficient accuracy as close to T_c as possible.

Result for Ferroelectric Transitions Interest in the phenomenon of ferroelectricity led to a number of investigations on the electrical and thermal properties of ferroelectrics[12]. Electrical measurements of high accuracy have been carried out on a large number of substances. However the earlier thermal measurements have not been precise. Considerable discrepencies are found among them both in detail and shape of the curves close to the transition.

Recently high resolution studies, especially on specific heats of a number of ferroelectric materials, suggest logarithmic or other singularities near T_c. A logarithmic infinity at the transition temperature is reported in specific heats of triglycine sulphate[13], potassium dihydrogen phosphate[14], potassium dihydrogen arsenate[14] and antimony sulphur iodide[15].

The specific heat of sodium nitrite also indicates the presence of a strong singularity at the Curie temperature[16, 17]. Therefore as in ferromagnetic/antiferromagnetic to paramagnetic transitions[4], in the case of transitions in ferroelectrics or antiferroelectrics also, the conventional method of making correlations based on Eherenfest relations, often found even in current literature, is unsound. These infinities render equation [1] invalid and in such cases any agreement between experimental and calculated values of DT/DP should be considered as largely fortuitous. The more general scheme of Pippard's relations should be employed for making these correlations and estimating the values of DT/DP.

Detailed specific heat measurements near T_c have been made on a relatively large number of substances, whereas high resolution studies on thermal expansion or elastic behaviour are available only for a limited number of substances, like triglycine sulphate, sodium nitrite, barium titanate, lead titanate and *KDP*. In the present note a detailed discussion is given of these materials.

TRIGLYCINE SULPHATE

The crystals of triglycine sulphate belong to monoclinic system and the Curie temperature is about 49°C. The polar room temperature phase belongs to the space group $P2_1$ which is transformed into the space group $P2_1/m$ on transition to the paraelectric phase. Investigation of dielectric and thermal properties established the transition to be of the second order[18].

The early specific heat data showed only a hump near T_c and did not give any indication of a singularity. Recently careful investigations by Strukov[19] have shown a logarithmic singularity both above and below the Curie temperature[13]. However for some time a controversy had existed over the values of thermal expansion coefficients. Ezhkova and coworkers[20], using X-ray lattice parameter measurements, and Ganesan[21] using interferometric measurements, reported values along *a* and *b* axes which disagreed seriously in magnitude, sign and temperature variation. Therefore Shibuya and Hoshino[22] carried out detailed measurements using both X-ray and dilatometric methods. They found agreement with Ganesan's data along the *b*-axis (α_b negative and becoming more negative as T_c is approached from below) and with the Russian data along the *a*-axis (α_a negative and becoming more negative as T_c is approached from lower temperatures). Telle[23] has also recently measured the thermal expansion coefficients. The trend of values completely agrees with the results of Shibuya and Hoshino. It must therefore be concluded that Ganeshan's results along *a*-axis and the results of Ezhkova *et al* along the *b*-axis contain unsuspected errors.

In the present discussion, the specific heat data were taken from the logarithmic fit given by Grindlay[13]. The volume expansion coefficients were obtained from the recent work of Telle[23] who has given the linear expansions along three mutually perpendicular directions. The exact values[21] of the Curie temperature are slightly different in the reports of the various workers, probably because of the small influence of crystal perfection and purity. Hence C_p and β values were taken for specific $|T_c - T|$ intervals in the low temperature side of the transition.

The C_p versus β plot shown in the Figure 1 is linear in the vicinity of T_c. The value of DT/DP calculated from the asymptotic slope is +1.8°C/*k*bar with an error of about 10%. This is in agreement with the experimental value of 2.6°C/*k*bar obtained by Jona and Shirane[24] in their studies upto 2500 atm., 2.6°C/*k*bar obtained by Leonidova and co-workers[25] in their studies upto

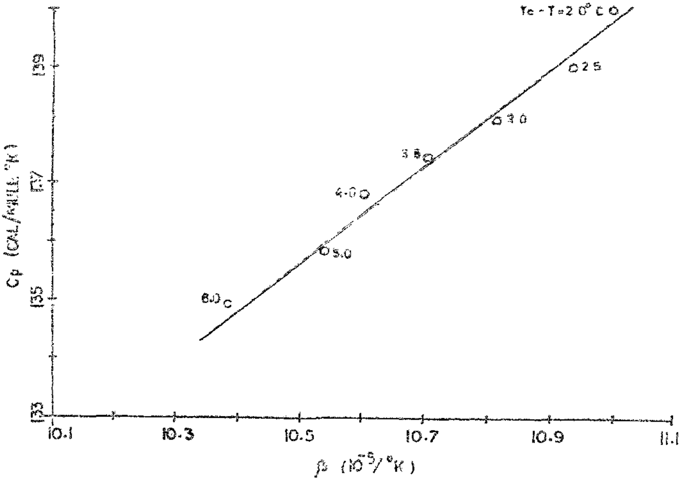

FIG. 1

The plot of heat capacity C_p as a function of volume expansion coefficient β for triglycine sulphate. Values of T_c-T are shown in °C near the points.

5000 atm, and with the value 1·6°C/*k*bar obtained by Zheludev and co-workers[26]. The experimental values of DT/DP are invariably obtained from the measurement of dielectric properties at high pressures.

The correlation of elastic compliances and specific heat of triglycine sulphate was recently reported by Janovec[11]. Data on only three elastic compliances S_{11}, S_{22} and S_{33} are available close to the transition[27]. These are all adiabatic values, but the difference between adiabatic and isothermal values is insignificant for the present purpose. In view of the uncertainty in the thermal expansion data available then, Janovec used equation [9] relating S_{ij} to C_p rather than checking equation [7] connecting S_{ij} and α_i. Taking the diagonal terms in equation [9] we have

$$S_{11}^{T} = \gamma_1^2 (C_p/vT) + \text{constant} \qquad [10]$$

$$S_{22}^{T} = \gamma_2^2 (C_p/vT) + \text{constant} \qquad [11]$$

$$S_{33}^{T} = \gamma_3^2 (C_p/vT) + \text{constant} \qquad [12]$$

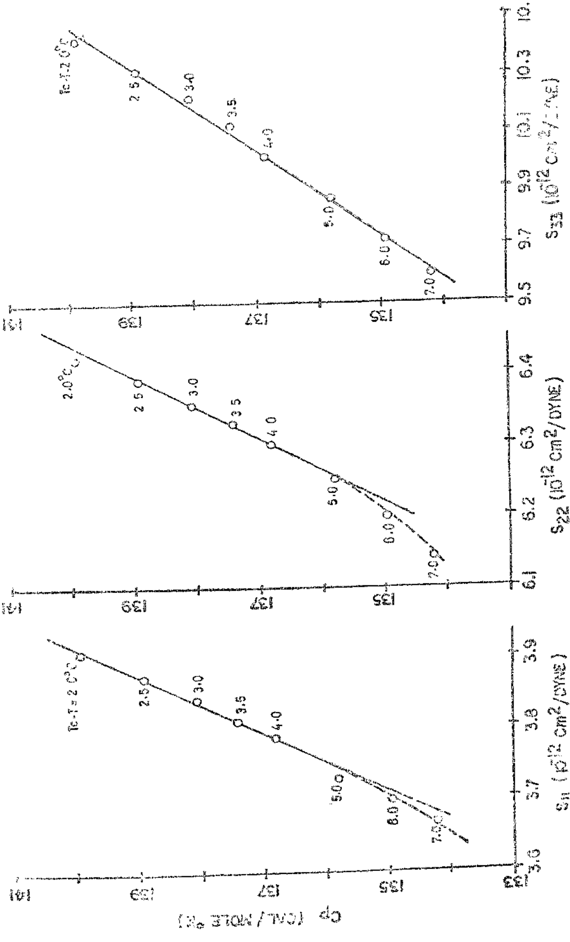

FIG. 2

Plots of heat capacity C_p as a function of elastic compliance coefficients S_{ii}'s for T.G.S. Values of $T-T_c$ are shown in °C near the points.

The plots of S_{11}, S_{22} and S_{33} as a function of C_p are shown in Figure 2. S_{22} represents the compliance coefficient along b-axis, the two fold symmetry axis while S_{33} is the compliance coefficient along the axis 3 coinciding with the c-axis and S_{11} that along axis 1 which is perpendicular to 3. Telle, in his thermal expansion studies, has chosen the axis 1 to coincide with the a-axis and the axis 3 perpendicular to axis 1. The plots of S_{ii}'s as a function of C_p are approximately linear, according to the above equations. The values of γ_1, γ_2 and γ_3 calculated from the asymptotic slopes of these plots are $\gamma_1 = -8.0$, $\gamma_2 = -8.2$ and $\gamma_3 = +14.9$ in units of $10^{-3}\,^\circ C/\text{bar}$. The corresponding values given by Janovec are -7.1, -9.3 and $+13.9$ in the same units. We have corrected the signs of Janovec's values in the manner described below Within the accuracy of about 10% in both sets, the agreement with Janovec's values is fair; the slight differences arise because asymptotic slopes have been taken in the present work, whereas Janovec gives equal weightage to the points far away from T_c.

It should be noted that γ_i's calculated from the equations [10] – [12] can be positive or negative. Janovec erroneously gives positive sign to all the γ_i's and obtains a very large value for DT/DP $(= \Sigma \gamma_i) = 30{\cdot}3 \times 10^{-3}\,^\circ\text{C/bar}$. The correct procedure, obviously, is to employ equations 6 and 7 qualitatively to find the true sign of γ. In the present case for $T < T_c$, C_p, S_{11}, S_{22} and S_{33} steadily increases with T The linear expansion coefficient α_3 (thermal expansion coefficient perpendicular to the axis 1) also increases with T, while α_1 and α_2 decrease with T as the transition is approached from below. Therefore γ_1 and γ_2 have negative signs while γ_3 has positive sign. (Here it must again be pointed out that the two perpendicular axis 1 and 3 in the a-c plane used in the thermal expansion studies and elastic studies do not exactly coincide. Still the correct signs for γ_i can be known from the trend of curves in Ganesan's[21] work which, in addition to the three perpendicular directions, gives the expansion coefficient along the c-axis which is the axis 3 chosen in elastic studies).

The plots as in figure 2, while giving an estimate of the change of T_c with uniaxial stresses, are not suitable for evaluating DT/DP because the latter is equal to $\gamma_1 + \gamma_2 + \gamma_3$ and is hence obtained as the difference between two large quantities. Thus with correct signs for γ_i, DT/DP comes out as $-1{\cdot}3 \times 10^{-3}\,^\circ\text{C/bar}$ with an error of about $\pm 2 \times 10^{-3}\,^\circ\text{C/bar}$. Therefore no reliable estimate of DT/DP can be made from the values of γ_i in the present case. More accurate values of S_{ij} very close to T_c will be needed for a realistic comparison with the experimental determination of DT/DP. The value $DT/DP = 30{\cdot}3$ as given by Janovec is high by an order of magnitude compared to the experimental values of 2.6 and 1·6 (× $10^{-3}\,^\circ\text{C/bar}$) and the error arises from the wrong signs of γ_i. (It must also be pointed out that there is a slip in Janovec's work. He puts $\gamma_i = -DT/DX_i$ and still gives $DT/DP = -\sum_{i=1}^{3} \gamma_i$ instead of $DT/DP = \Sigma\, \gamma_i$).

SODIUM NITRITE

Sodium Nitrite belongs to the space group Im 2m at room temperature. The polar phase transforms to centro-symmetric space group Immm at about 163°C. Various physical properties such as dielectric, thermal, optical and other properties have been extensively studied by the Japanese workers.

The X-ray studies[28] just above Curie temperature showed an anomalous temperature dependence of lattice constants. It was therefore concluded that a phase intermediate between the ferroelectric and paraelectric phases should exist. This was later confirmed by the specific heat measurements[16, 17], study of electrical properties as a function of temperature and pressure[31] and and X-ray studies[32]. On the basis of X-ray intensities it is concluded that the intermediate phase is antiferroelectric with a sinusoidal modulation of the moment, unlike the usual antiparallel modulation The transition at 163°C corresponds to the transition from ferroelectric to antiferroelectric phase while the transition at 164°C occurs from sinusoidal to the usual paraelectric phase.

Considering first the transition at 163°C between the ferroelectric and antiferroelectric phases, the observation of a doubled hysteresis loop in the dielectric measurements[33], volume discontinuity[17] at the transition and the observation of latent heat[34] leave no doubt that the transition is of the first order. Of course irrespective of the order of transition, correlations between C_p, β and k_T can be carried out using the Pippard scheme.

The thermal expansion data of Maruyama and Sawada[30] are of high resolution and cover the region $T_c - T \leq 2°$ in detail. Therefore it is possible to check equation 6 connecting C_p and α_i and obtain the variation of T_c with uniaxial stresses. The specific heats below T_c are taken from the work of Sakiyama and co-workers[17] and the C_p vs α_i plots are given in figure 3. The crystal axes used are those of Maruyama and Sawadea[30]. There is reasonable linearity close to T_c and it is obtained that $\gamma_1 = +3.4$ mdeg/bar; $\gamma_2 = +4.0$ mdeg/bar; $\gamma_3 = -2.0$ mdeg/bar. The individual values of γ_i have not been determined experimentally but DT/DP has been measured as 4.9×10^{-3} °C/bar by Gesi and co-workers[31] in their high pressure studies upto 10 k bar. These authors have also estimated $DT/DP = 5.0 \times 10^{-3}$ °C/bar from the Clausius – Clapeyron equation. The present value of $DT/DP (= \Sigma \gamma_i)$ is 5.4×10^{-3} °C/bar. Considering the error about 10% in γ_i's this value is not in disagreement with the experimental results.

The measurements of elastic constants has not been done to a high enough resolution. Nevertheless using the results of Hamano and co-workers[35], curves have been drawn to check equations 10 – 12. The values of γ ($\gamma_1 = +1.8$ mdeg/bar; $\gamma_2 = 2.1$ mdeg/bar; $\gamma_3 = -2$ mdeg/bar) are less reliable than the values given above from the high resolution thermal expansion data.

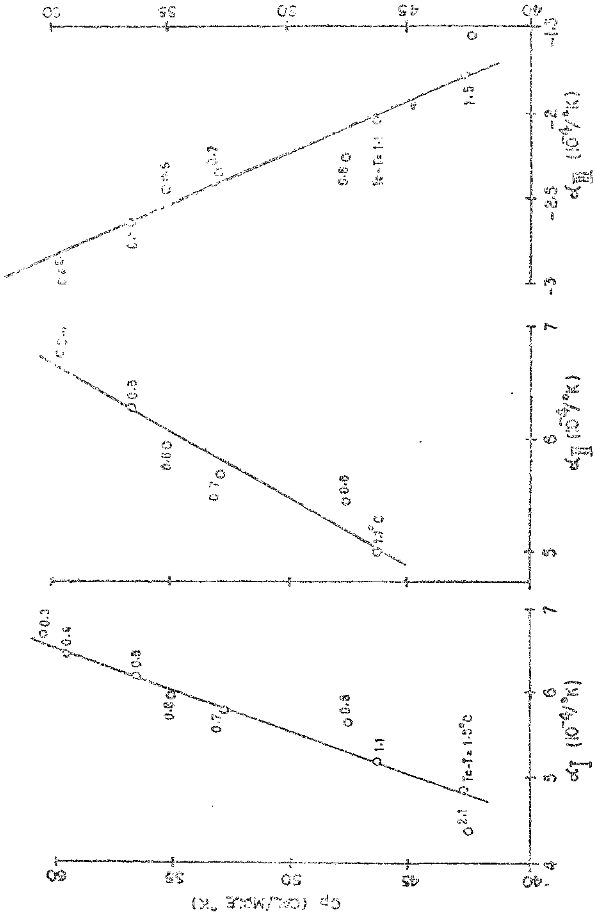

FIG. 3

Plots of heat capacity C_p as a function of principal thermal expansion coefficients for NaNO$_2$. Values of $T_c - T$ are shown in °C near the points.

(The slopes for the plots C_p vs. α_I and C_p vs. α_{II} are positive while the slope for C_p vs. α_{III} is negative.)

The transition from the sinusoidal antiferroelectric to para-electric phase at 164.5 °C is probably of the second order. The experimental value[31] of DT/DP is +5.6 °C/kbar. Reliable measurements of β and k_T close enough to the transition are not available and so it has not been possible to apply Pippard's scheme to discuss this transition.

POTASSIUM DIHYDROGEN PHOSPHATE

The room temperature paraelectric phase of potassium dihydrogen phosphate belongs to the tetragonal system with space group $F\bar{4}d2$. This transforms at 123°K into ferroelectric phase with orthorhombic symmetry, space group $Fdd2$.

The heat capacities of *K D P*, deuterated *K D P* and potassium dihydrogen arsenate were measured over a wide range of temperature by Bantle[36]. Zwicker and Scherrer[37], Stephenson and Hooley[38] and Mendelssohn and Mendelssohn[39] determined the specific heat of *K D P* and found overall agreement among their values. Using these specific heat data, Grindlay[14] showed that the specific heats of *K D P* and *K D A* show a logarithmic singularity at the Curie point.

Arx and Bantle[40] have measured the expansivity close to T_c and find that along one of the orthorhombic axes X_1', which is rotated through 45° relative to the original X_1 axis of the tetragonal system, there is a sharp contraction close to the transition. The behaviour of the thermal expansivity along the other two axes of the orthorhombic system in the ferroelectric phase has not been specifically mentioned. The coefficients of thermal expansion from their observations plotted against C_p values taken from the work of Stephenson and Hooley are shown in figure 4. The linear fit gives $\gamma_1' = -1.43 \times 10^{-3}$ deg/bar which gives an estimate of the change of Curie point with uniaxial stress along the X_1' direction. Since the behaviour of thermal expansion along the other two orthorhombic axes has not been studied in such detail[41] it is not possible to predict quantitatively the effect of hydrostatic pressure on the Curie point of *K D P*. Qualitatively a decrease of T_c with increase of pressure can be predicted. At present there is no experimental observation of DT/DP.

BARIUM TITANATE AND LEAD TITANATE

The room temperature polar phase of barium titanate belongs to the tetragonal system, space group P 4 mm. Above the Curie point (120°C) the symmetry on non-polar phase is cubic, space group P m 3 m. The ferroelectric to paraelectric phase transitions of the $BaTiO_3$ group of substances are of the first order and therefore Clausius-Clapeyron equation can be directly applied to obtain the value of DT/DP. All the same the specific heat and thermal expansion show rather large values as T_c is approached and therefore it is of interest to discuss briefly C_p and β in the Pippard scheme.

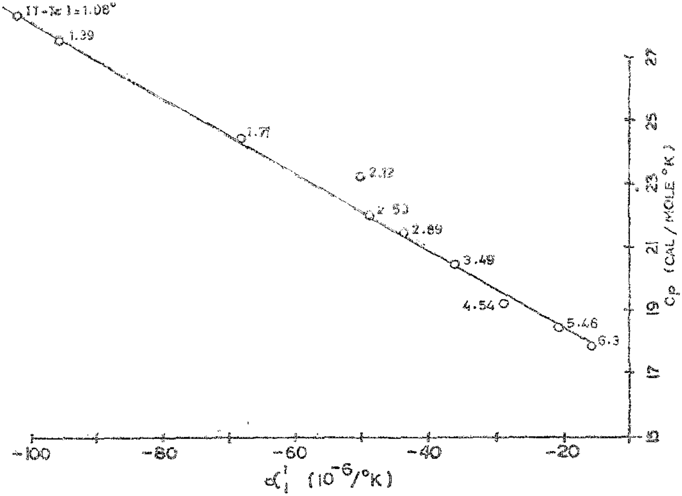

FIG. 4

The plot of heat capacity C_p as a function of linear thermal expansion coefficient α_1' along one of the crystallographic axis of the orthorhombic phase for KH_2PO_4. Values of T_c-T in °C corresponding to various points are shown. The slope is negative.

There have been many studies on the properties of barium titanate, lead titanate, strontium titanate and their mixtures in order to understand the mechanism of ferroelectricity in perovskites[12]. Since impurities affect the phenomena very near T_c, it appears best to restrict the discussion to pure materials.

The C_p versus β plot of $BaTiO_3$ was made using the specific heat and thermal expansion coefficient values Shirane and Takeda[42] measured on the same sample. The Curie temperature is found to decrease with pressure (Fig. 5) which is in agreement with the experimental result. The asymptotic slope of the plot gives DT/DP equal to -5.8°C/kbar. The value obtained[42] from applying Clausius-Clapeyron equation, in which the heat of transition is estimated from the specific heat data, is -6.7°C/kbar. The use of directly measured value of latent heat will be desirable.

The experimental value of DT/DP for $BaTiO_3$ has been determined by several workers from dielectric behaviour at high pressures. It is important

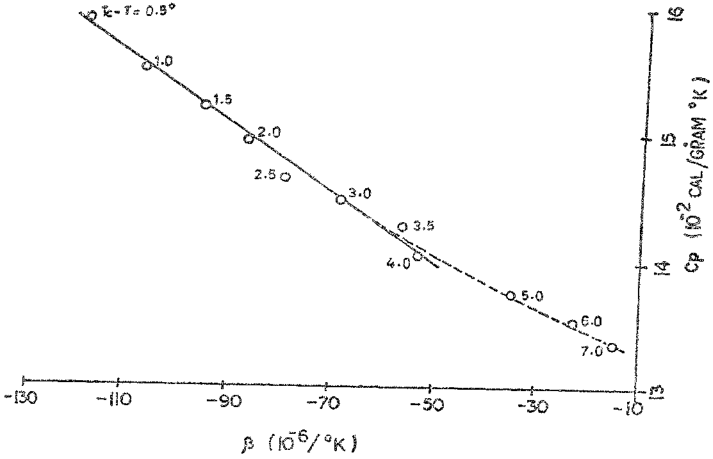

FIG. 5

The plot of heat capacity C_p as a function of volume expansion coefficient β far $BaTiO_3$. Values of $T_c - T$ corresponding to various points in the plot are indicated. The slope is negative

that only the initial slope is taken because DT/DP changes sign at about 3.5 kbar[43-45]. The experimental values, obtained from the initial slope are -5.8°C/kbar[46], -4.3°C/kbar[44] and -6.3°C/kbar[47]. Recently Samara[48] has obtained a range of values from -4.6 to -5.9°C/kbar for different samples. The large scatter in the experimental values is due to the dependence of DT/DP principally on sample purity and to a lesser extent on domain structure. In view of these variations, the value -5.8°C/kbar obtained from the Pippard relation should be considered satisfactory.

The C_p versus β plot of lead titanate (Fig. 6) is obtained using the same sample of $PbTiO_3$ by Shirane and Takeda[49]. A value of DT/DP equal to $-3x\,10^{-3}$ °C/kbar is predicted. At present there is no experimental measurement of this quantity in lead titanate.

DISCUSSION

The Pippard method of correlating the thermal data of ferroelectric substances near the transition temperature is applicable irrespective of the order or the nature of the transition involved. The Ehrenfest relations turn

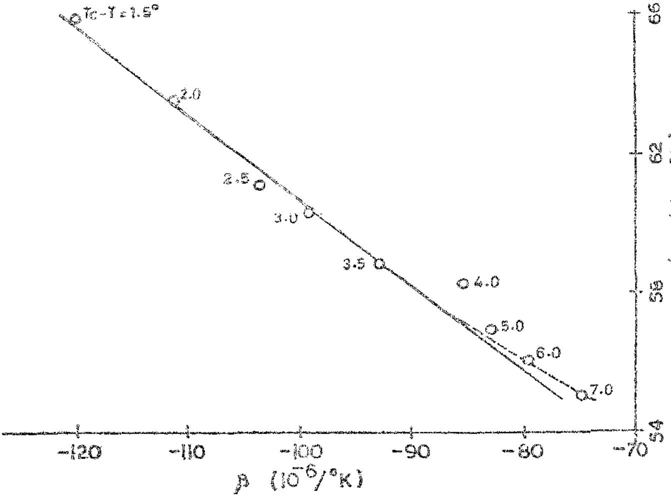

FIG. 6

The plot of heat capacity C_p as a function of volume expansion coefficient β for $PbTiO_3$. Values of $T - T_c$ corresponding to various points in the plot indicated. The slope is negative.

out to be special cases of this general scheme, and of course for λ – type transition only the present method applies. Moreover, the Pippard relations refer to a single phase and this is an advantage in discussing the experimental results.

Accurate thermal and compressibility data near T_c are available for only a few ferroelectric substances and therefore it is not possible to carry out any detailed correlation among the thermodynamic quantities. Furthermore, the correlations reported here are for the polar phase occurring below T_c, because accurate thermal expansion data for the phase above T_c are not available. It is well known that if the data in the phase above and below T_c are used for obtaining these plots, the asymptotic slope and hence DT/DP can be estimated to a high degree of accuracy.[1] It is, however, abundantly clear from the examples cited here that the Pippard relations are borne out at the ferroelectric transitions. The values of the rate of change of Curie point with pressure estimated from the Pippard relations agree fairly well with the directly measured values.

In case of barium titanate, data on the samples of different purity support the contention that the purity of the sample is of vital importance in determining the shape and singularity of the thermodynamic properties at the transition. For instance, the values of DT/DP on the samples of different purity[8] range from -4.6 to -5.9°C/kbar. Data on the purity and thermal history of the samples employed in the present correlations have not always been quoted in the original publications. It is most desirable that all the thermal and elastic properties as well as DT/DP be measured on the same sample; and in order to determine the effects of impurities, for the same substance on the samples of different impurity. At present such data are generally lacking in ferroelectric materials.

The available specific heat data on the ferroelectric substances are on the whole more abundant and accurate that β or k_T data. This brings out the dire need of detailed studies on these physical properties on a large number of ferroelectric substances. A programme of work along these lines is being initiated here with the financial assistance of CSIR.

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NOTE ADDED IN PROOF

Very recently Cook[a] has carried out thermal expansion measurements in KH_2PO_4 crystals both above and below T_c. He has reported expansivity curves along the orthorombic *c*-axis and as average of the other orthorhombic axes a' and b'. Plotting the volume expansion coefficient β calculated from Cook's data against the specific heat data of Stephenson and Hooley[38] (as already reported) we have obtained the value of DT_c/DP as $-4\ 8$ *m*. deg/bar. Very recently, fresh experimental measurements on the effect of hydrostatic pressure on the Curie temperature of KH_2PO_4 by Hegenbarth and Ullwer[b] show the value of DT_c/DP as -5.7×10^{-3} and -5.5×10^{-3} deg/bar, using three different specimens. Umebayshi[c] *et al.*, have reported a value of $-4.52 \pm 0.06°C/k$.bar. for DT_c/DP. In the light of such varied values for DT_c/DP, the value obtained through Pippard scheme must be considered satisfactory.

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