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Pippard's relations applied to certain λ transitions in dielectric and magnetic materials

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Abstract. When making thermodynamically based comparisons concerning behaviour in the vicinity of Curie points or Néel points, Pippard's relations are in principle more pertinent than Ehrenfest's. In a discussion supplementing the analyses of Sawatzky and Bloom, and Skalyo, Cohen, Friedberg and Griffiths, various magnetic Pippard's relations are considered, and it is re-emphasized that a relation derived by Fisher in statistical mechanical terms (that near an antiferromagnetic Néel point the rise in specific heat closely follows the *temperature coefficient* of the magnetic susceptibility) amounts very nearly to a relation of the purely thermodynamic type obtained by Pippard for λ transitions generally. Relevant observations are analysed in such terms for a number of representative cases, and comparisons made with the dependence of λ temperatures on hydrostatic pressure and magnetic field. On the whole, the results of such a treatment confirm the utility of following the relatively few previous analyses along such lines.

Correspondingly, for λ transitions associated with a very rapid change of dielectric properties with temperature, the λ temperature corresponds to a peak in the derivative of electric susceptibility with respect to temperature, and not to a maximum in the susceptibility itself.

1. Introduction

Various discussions have been given from a thermodynamic standpoint of behaviour near a magnetic λ transition, with reference to the dependence of the λ temperature on pressure and on field. The earlier work on the effect of hydrostatic pressure on ferromagnetic and ferroelectric Curie points was reviewed by Bradley (1963), and Bloch and Pavlovic (1969) have given an extensive review of investigations on ferromagnetic Curie points and antiferromagnetic Néel points at high pressures. In the work there reviewed, most of the thermodynamic comparisons that have been made have been based on Ehrenfest's equations, and as such rest on a foundation that is in principle inappropriate: these λ transitions, as Bloch and Pavlovic to some extent point out, do *not* genuinely exhibit finite discontinuities in C_p , in the coefficient of expansion, or in the isothermal compressibility.

Save for the very careful analysis of behaviour near *ferroelectric* Curie points by Janovec (1966), there seems to have been surprisingly little attempt to employ Pippard's (1956, 1957) thermodynamic relations

$$\frac{C_p}{T} \simeq \text{constant} + \left(\frac{dp}{dT} \right)_\lambda \left(\frac{\partial V}{\partial T} \right)_p \quad (1)$$

and

$$\left(\frac{\partial V}{\partial T}\right)_p \simeq \text{constant} + \left(\frac{dp}{dT}\right)_\lambda \left(-\frac{\partial V}{\partial p}\right)_T \quad (2)$$

instead of Ehrenfest's in the discussion of λ transitions dependent on magnetic or electric fields. There have been exceptions. For several antiferromagnetic Néel points Janusz (1960, quoted by Bloch and Pavlovic 1969) seems to have employed an argument along the lines of that of Kuper (1955) to estimate the slope of the λ line $(dp/dT)_\lambda$ as $(C'_p - C''_p)/VT'_\lambda(\alpha' - \alpha'')$ (where the superscripts prime and double prime indicate values at two neighbouring points lying to the same side of T'_λ , and α is the coefficient of expansion); which amounts very nearly to the use of (1). Following Janovec (1966), Gonano *et al* (1968), in connection with the thermal expansion of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ near its antiferromagnetic Néel point, have made an explicit use of Pippard's relations quite unusual in such work. The analysis given by Argyle *et al* (1967) for EuO was somewhat similar.

Certain magnetic analogues of Pippard's relations have been inferred (by an argument similar to that of Buckingham and Fairbank 1961) and applied by Sawatzky and Bloom (1962, 1964) and Skalyo *et al* (1967) to the dependence of antiferromagnetic Néel temperatures on magnetic field, and various Pippard's relations have been derived by Janovec (1966) for ferroelectric Curie points. However, some of the more useful forms of the actual magnetic Pippard's relations seem never to have been given explicitly. They are readily inferred from standard thermodynamic relations for magnetic fields, by the same kind of argument (Pippard 1956, 1957 and cf Rice 1954) which leads to the ordinary Pippard's relations.

The underlying argument being based exclusively on macroscopic thermodynamic theory, the applicability of the relations will not be restricted to λ transitions whose microscopic interpretation is in terms of antiferromagnetism. In particular, some such relations would at least in principle be expected to apply just above a ferromagnetic Curie point. In this context, however, the approximation of Pippard's relations may be less satisfactory, in as much as peaks in specific heats often rise less sharply at ferromagnetic Curie points than at antiferromagnetic Néel points.

In what follows, the discussion will be concerned first with formulating the various Pippard's relations for magnetic λ transitions, then with the application of the original relations to the dependence of ferromagnetic Curie temperatures and antiferromagnetic Néel temperatures on hydrostatic pressure, and with the application of Pippard's relations couched in terms of magnetic properties, together with a comparison with a very similar result derived by microscopic arguments by Fisher (1962).

Finally, some attention is given to λ transitions accompanied by a very rapid dependence of dielectric properties on temperature. Following on the work of Janovec (1966), which presented generalized Pippard's relations with special reference to ferroelectric Curie points, the present discussion is concerned primarily with other sorts of 'dielectric λ transitions'.

2. Pippard's relations for magnetic λ transitions

Consider a system in the vicinity of a λ transition near which magnetic properties vary rapidly with temperature, but excluding conditions (if any) in which ferromagnetism is exhibited. For simplicity, let the system considered be an isotropic specimen (of magnetic moment M) in the form of a long thin rod parallel to the magnetic field.

The independent variables may be taken to be the temperature, the pressure and the square of the magnetic field. Then the appropriate generalization of the approximation used by Pippard (1956, 1957) is to assume that apart from a smoothly varying part, approximately quadratic in the independent variables, $U + pV - TS - HM$ is equal to a function $\phi(\eta p - T + \zeta H^2)$ of $(\eta p - T + \zeta H^2)$ alone, where η, ζ are constants to be identified respectively with $(\partial T_\lambda / \partial p)_H$ and $(\partial T_\lambda / \partial (H^2))_p$.

Then the three first derivatives of $U + pV - TS - HM$, with respect to p, T , and H^2 , take the form $[V, -S, -\frac{1}{2}\chi] \simeq [\text{linear term} + \eta\phi', \text{linear term} - \phi', \text{linear term} + \zeta\phi']$ where $\chi \equiv M/H$ is the magnetic susceptibility (i) referred to a given quantity of specimen and not to a given volume, and (ii) defined as magnetic moment divided by field and not as a differential susceptibility. The Hessian matrix of second derivatives

$$\begin{pmatrix} (\partial V / \partial p)_{T,H} & -(\partial S / \partial p)_{T,H} & -\frac{1}{2}(\partial \chi / \partial p)_{T,H} \\ (\partial V / \partial T)_{p,H} & -(\partial S / \partial T)_{p,H} & -\frac{1}{2}(\partial \chi / \partial T)_{p,H} \\ (\partial V / \partial (H^2))_{T,p} & -(\partial S / \partial (H^2))_{T,p} & -\frac{1}{2}(\partial \chi / \partial (H^2))_{T,p} \end{pmatrix}$$

is then to be taken as approximately equal to

$$\begin{pmatrix} \text{constant} + \eta^2 \phi'' & \text{constant} - \eta \phi'' & \text{constant} + \eta \zeta \phi'' \\ \text{constant} - \eta \phi'' & \text{constant} + \phi'' & \text{constant} - \zeta \phi'' \\ \text{constant} + \eta \zeta \phi'' & \text{constant} - \zeta \phi'' & \text{constant} + \zeta^2 \phi'' \end{pmatrix}.$$

It then follows that:

$$\left(\frac{\partial \chi}{\partial T} \right)_{p,H} \simeq \text{constant} - 2\zeta \left(\frac{\partial S}{\partial T} \right)_{p,H} = \text{constant} - 2 \left(\frac{\partial T_\lambda}{\partial (H^2)} \right)_p \frac{C_{pH}}{T} \quad (3)$$

$$\left(\frac{\partial V}{\partial (H^2)} \right)_{T,p} \simeq \text{constant} - 2\zeta \left(\frac{\partial V}{\partial T} \right)_{p,H} = \text{constant} - 2 \left(\frac{\partial T_\lambda}{\partial (H^2)} \right)_p \left(\frac{\partial V}{\partial T} \right)_{p,H} \quad (4)$$

$$\left(\frac{\partial \chi}{\partial (H^2)} \right)_{T,p} \simeq \text{constant} - \zeta \left(\frac{\partial \chi}{\partial T} \right)_{p,H} = \text{constant} - \left(\frac{\partial T_\lambda}{\partial (H^2)} \right)_p \left(\frac{\partial \chi}{\partial T} \right)_{p,H} \quad (5)$$

(three relations of approximate linearity in the neighbourhood of the λ transition, indicating graphs whose slopes would give estimates of the dependence of T_λ on field); two relations which are the original Pippard's relations (1) and (2); and

$$\left(\frac{\partial \chi}{\partial T} \right)_{p,H} \simeq \text{constant} + \frac{2}{\eta} \left(\frac{\partial V}{\partial (H^2)} \right)_{T,p} = \text{constant} + \frac{2}{(\partial T_\lambda / \partial p)_H} \left(\frac{\partial V}{\partial (H^2)} \right)_{T,p} \quad (6)$$

(a relation of approximate linearity between magnetic properties, but which would furnish an estimate of the dependence of T_λ on hydrostatic pressure).

As is well known in the case of the ordinary Pippard's relations, any such relation is approximate, and not exact. Approximations were made in the argument in treating

the slowly varying part of $U + pV + TS - HM$ as only a quadratic function of the independent variables, and in treating the more rapidly varying part as a function of the single variable $(\eta p - T + \zeta H^2)$ with η, ζ taken as being constant.

3. Effect of hydrostatic pressure on Curie temperatures and Néel temperatures

In view of the surprising persistence (despite the work of Janovec 1966) of the use of Ehrenfest's relations instead of Pippard's, the few previous investigations using the latter have been supplemented by constructing a number of Pippard plots for some other substances exhibiting ferromagnetic Curie points and antiferromagnetic Néel points, and the slopes compared with what is known about the dependence of the relevant T_λ on hydrostatic pressure.

3.1. Ferromagnetic Curie points

3.1.1. *Nickel*. A plot of C_p/T against $(\partial V/\partial T)_p$ has been constructed (figure 1) from the data of Handler *et al* (1967) on the specific heat, and of Nix and MacNair (1941) on the thermal expansion. Other determinations of C_p (Moser 1936, Sykes and Wilkinson

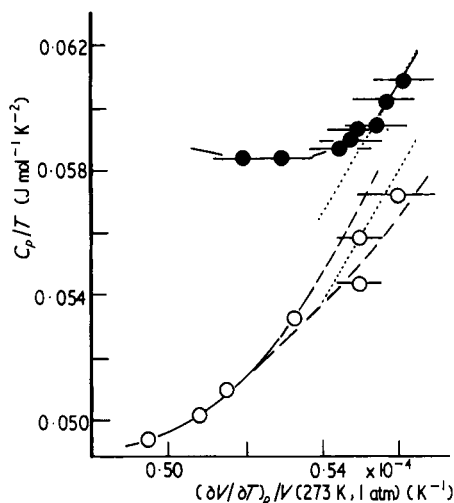


Figure 1. Ordinary Pippard plot for nickel around its ferromagnetic Curie point. ● Points for temperatures below T_λ (about 0 to 18 K below); ○ points for temperatures above T_λ (1 to 30 K above). Dotted lines have slopes corresponding to the *observed* dependence of Curie temperature on pressure.

1938, Néel 1938, Pawel and Stansbury 1965 and Kraftmakher 1966) give similar but less well defined plots. Both the plot for temperatures above T_λ , and that for temperatures below, exhibit distinct curvature. The steepest and most relevant portions (where the points are those for the temperatures closest to T_λ) have slopes corresponding to values of dT_λ/dp

$$\begin{aligned}
 &+0.3_4 \text{ K kbar}^{-1} && \text{(points for } T < T_\lambda) \\
 &+(0.4 \pm 0.1) \text{ K kbar}^{-1} && \text{(points for } T > T_\lambda)
 \end{aligned}$$

as compared with the direct experimental value (Bloch and Pauthenet 1965, Léger *et al* 1966a, Okamoto *et al* 1967b)

$$+(0.32 \pm 0.02) \text{ K kbar}^{-1}.$$

The numerical agreement, and the curvature of the plots, are not too unsatisfactory. The corresponding plot for liquid sulphur, a substance for which the graph of C_p against temperature looks qualitatively very similar to that for nickel, is linear only over a range of temperature around 6 K to one side of the maximum in C_p and about 1 to 2 K to the other (Klement 1966).

3.1.2. Iron. The experimental observations on iron are very puzzling. The Curie point is observed to be, within experimental error, independent of pressure (Patrick 1954, Léger *et al* 1966b). Yet the coefficient of expansion, as inferred from x ray data on the lattice spacing, changes rapidly around the Curie point, falling to quite small values (Esser *et al* 1938, Ridley and Stuart 1968). A contrary conclusion reached by other workers (Basinski *et al* 1955) is attributed by Ridley and Stuart to a taking of values at too widely separated temperatures. When combined with data on the specific heat (Kraftmakher and Romashina 1965, see also the compilation of Darken and Smith 1951), these x ray-inferred coefficients of expansion lead to the prediction of a dependence of Curie point on pressure *greater* than that for nickel, but in the opposite sense (a decrease). Such is in direct conflict with what is observed.

Old direct macroscopic investigations of the thermal expansion (Benedicks 1914) suggest that there *might* be a dip in the coefficient of expansion, but that *if* genuine such a dip appears only at temperatures somewhat below the Curie point. If such is the case, then the previous puzzle disappears; but only to be replaced by another, that of how macroscopic and microscopic thermal expansions can differ so remarkably.

3.1.3. Europium monoxide. Argyle *et al* (1967) found that for EuO the quotient (magnetoelastic contribution to the coefficient of linear expansion)/(magnetic contribution to C_p) was constant (equal to $(0.80 \pm 0.04) \times 10^{-6} \text{ mol J}^{-1}$), and inferred that $dT_\lambda/dp = 0.34 \pm 0.02 \text{ K kbar}^{-1}$. On reinterpreting their results by explicit use of the first Pippard's relation, an almost exactly equal estimate is obtained; in very satisfactory agreement with the experimental value (McWhan *et al* 1966, Sokolova *et al* 1966) of $0.4 \pm 0.1 \text{ K kbar}^{-1}$.

3.2. Antiferromagnetic Néel points

From very careful work on solid $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, it is clear (Gonano *et al* 1968, Dixon and Rives 1969) that near the Néel temperature (1.62 K) the specific heat and coefficients of expansion satisfy the first Pippard's relation (1). These studies did not examine any relation to the dependence of T_λ on hydrostatic pressure.

Data for some other substances will be considered here, in relation to the magnitude of dT_λ/dp .

3.2.1. Manganese monoxide. For solid MnO (Néel temperature 118 K) the specific heat was examined by Millar (1928) and Todd and Bonnicksen (1951), and the thermal expansion by Foëx (1948). A plot of C_p/T against the coefficient of expansion (figure 2) is somewhat curved. The point closest to T_λ lies well above the curve, but this may well be a consequence of greater accuracy in delimiting the peak in C_p than in delimiting that in α . A plausible straight line, through what might be the most reliable part of the

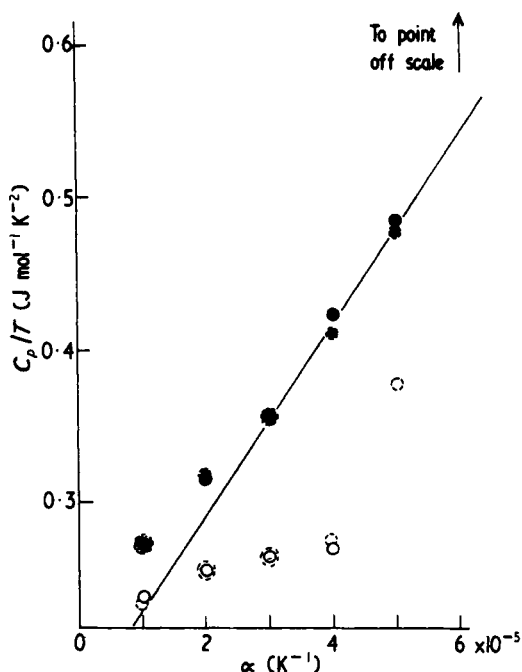


Figure 2. Ordinary Pippard plot for MnO around its antiferromagnetic Néel point. Points as in figure 1, 'complete' for C_p as measured by Todd and Bonnickson, 'broken' for those as measured by Millar. Ranges of temperature 78 K to 118 K, and 118 K to 132 K.

plot, has a slope corresponding to $dT_\lambda/dp \approx +0.2_1 \text{ K kbar}^{-1}$; Janusz' (1960, quoted by Bloch and Pavlovic 1959) estimate was $+0.3 \text{ K kbar}^{-1}$, and the experimental value (Bartholin *et al* 1967) is $+(0.30 \pm 0.02) \text{ K kbar}^{-1}$.

3.2.2. *Iron 'monoxide' (nonstoichiometric)*. For solid 'FeO' (Néel temperature 188 K) the data on the specific heat are due to Millar (1929) and Todd and Bonnickson (1951), and those on the thermal expansion to Foëx (1948). A slight adjustment of the scales of temperature used by the various investigators seems necessary in order to bring their results into correspondence. When this is done, a plot of C_p/T against α (figure 3) gives very satisfactory linearity so far as the points for temperatures below T_λ are concerned. The slope corresponds to $dT_\lambda/dp \approx +0.5_8 \text{ K kbar}^{-1}$ from Millar's values for C_p , or $+0.7_2 \text{ K kbar}^{-1}$ from those of Todd and Bonnickson; in satisfactory agreement with the experimental value (Okamoto *et al* 1967a) of $+0.65 \text{ K kbar}^{-1}$.

3.3. Conclusion

Except for iron, each substance considered here exhibits a reasonably satisfactory agreement between the slope of an ordinary Pippard plot and the observed dependence of the Curie or Néel temperature on hydrostatic pressure. The utility of Pippard's approach to the thermodynamics of λ transitions, already clearly illustrated for λ transitions not basically dependent on magnetic or dielectric behaviour (Pippard 1956, 1957, Buckingham and Fairbank 1961, Hughes and Lawson 1962, Garland and Jones 1963, Garland 1964a, 1964b and Klement 1966), and for ferroelectric Curie points (Janovec 1966), is seen evidently to extend to ferromagnetic Curie points and antiferromagnetic

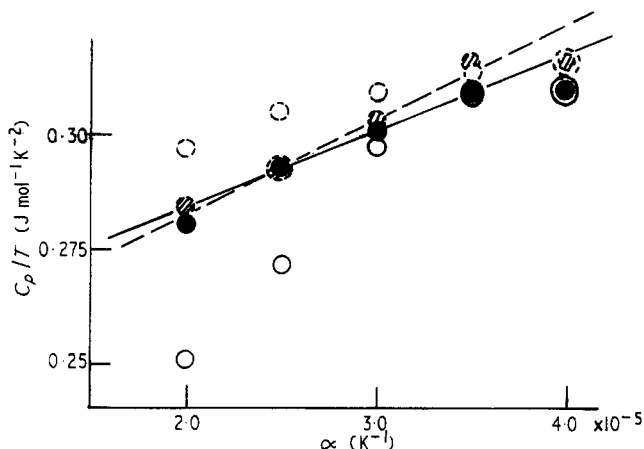


Figure 3. Ordinary Pippard plot for 'FeO' (nonstoichiometric) around its antiferromagnetic Néel point. Points as in figure 2. Ranges of temperature 164 K to 188 K, and 188 K to 193 K.

Néel points. As such, this kind of analysis (or some such similar procedure as that employed by Argyle *et al* 1967) should in future totally replace all appeal to Ehrenfest's relations when discussing effects of hydrostatic pressure on magnetic λ transitions.

4. Magnetic Pippard plots and the dependence of a Néel temperature on magnetic field

4.1. Plots of actual experimental data

Magnetic Pippard plots will be presented for two substances exhibiting antiferromagnetic Néel points; samarium (figure 4), for which the peak in the specific heat is relatively broad, and for which therefore the applicability of any kind of Pippard's relation might be considered dubious; and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (figures 5, 6 and 7), for which the peak in the specific heat rises very sharply.

No plots will be presented for metals just above a *ferromagnetic* Curie point. It turns out that, if plots of $(\partial\chi/\partial T)_{p,H}$ against C_{pH}/T are constructed, they are grossly curved, and can have a slope not even corresponding in sign with $(\partial T_\lambda/\partial(H^2))_p$. This initially surprising failure of a thermodynamically based relation may be interpreted as indicating that the λ line does not even approximate in slope to neighbouring contours of constant C_{pH}/T . Just above a ferromagnetic Curie point, $(\partial^2\chi/\partial T^2)_{p,H}$ is extremely large; which implies that C_{pH} must increase very drastically if a magnetic field is applied. Therefore, the locus of maxima may well differ considerably in slope from a contour of constant C_{pH}/T .

In this respect there appears to be a distinct contrast with *ferroelectric* Curie points. Garland and Novotny (1969) found an 'elastic Curie-Weiss law' to apply to KH_2PO_4 , and pointed out that this amounted to a dielectric Pippard's relation (cf Janovec 1966).

4.1.1. Samarium. A plot of corresponding values of $(\partial\chi/\partial T)_{p,H}$ and C_{pH}/T has been constructed (figure 4) for samarium, which has a Néel point close to 14 K. The data used are those of Lock (1957) for the magnetic susceptibility and of Roberts (1957) for the specific heat. The peak in the latter is not particularly sharp, so much so as barely

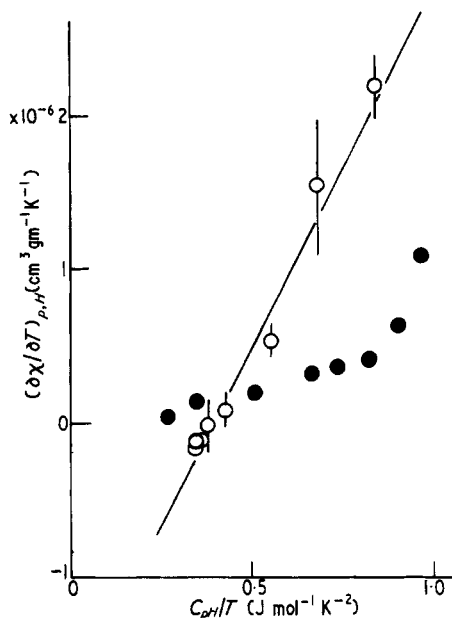


Figure 4. Magnetic Pippard plot for samarium around its antiferromagnetic Néel point. Corresponding values of $(\partial\chi/\partial T)_{p,H}$ and C_{pH}/T (for zero field). ● Points for temperatures below T_λ (10 K to 13.6 K); ○ Points for temperatures above T_λ (14 K to 18 K).

to qualify as indicating a λ transition. In view of this fact, it is very gratifying to find quite good linearity for the points for temperatures above the Néel point, and not too unsatisfactory that there is distinct curvature for the points for temperatures below.

4.1.2. Manganese dichloride tetrahydrate. The magnetic transitions in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Néel temperature 1.62 K) have been the subject of numerous extensive and careful investigations. The specific heat has been measured around T_λ both in the presence and in the absence of a magnetic field (Friedberg and Wasscher 1953, Voorhoeve and Dokoupil 1961, Dixon and Rives 1969, Reichert and Giaque 1969, Giaque *et al* 1970a, Giaque *et al* 1970c, Giaque *et al* 1970b). Magnetic properties have also been studied very thoroughly (Lasheen *et al* 1958, Gijsman *et al* 1959, Rives 1967, Reichert and Giaque 1969, Giaque *et al* 1970a, 1970b and 1970c), and related observations have been reported by McElearney *et al* (1969).

The peak in the specific heat rises up very sharply both from above and from below T_λ , and the data seem almost ideal for exhibiting a magnetic Pippard's relation. The magnetic data include susceptibilities measured with the field parallel to individual axes of a single crystal, and to each distinct susceptibility there corresponds a distinct Pippard's relation between $(\partial\chi/\partial T)_{p,H}$ and C_{pH}/T . For the susceptibility for a field parallel to the c axis (figure 5(c)), there is very good linearity for the points for temperatures below T_λ , but rather less satisfactory linearity for points for temperatures just above T_λ . For the susceptibility for a field parallel to the b axis (less strongly dependent on temperature), there is again very satisfactory linearity for the points for temperatures below T_λ ; and the two sets of points, for temperatures above and below T_λ , very nearly approach a common asymptote.

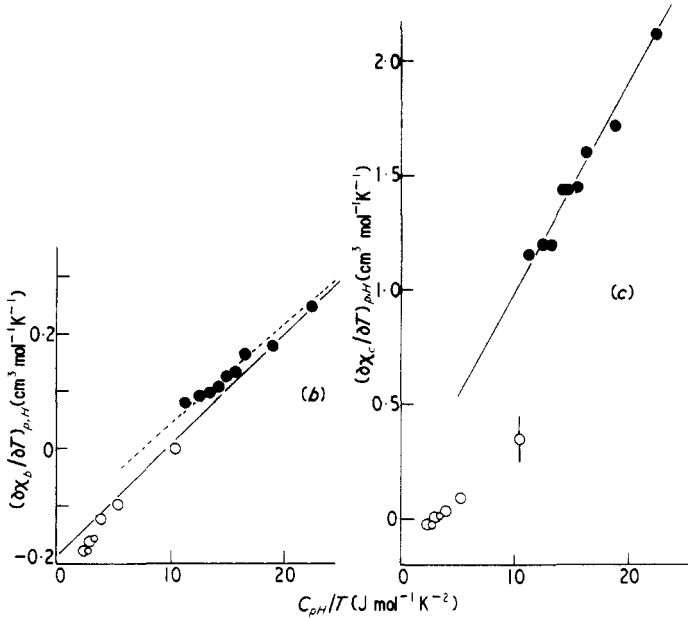


Figure 5. Magnetic Pippard plot for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ around its antiferromagnetic Néel point. Points as in figure 4 (range of temperature 1.38 K to 1.73 K): (b) for susceptibility for field parallel to *b* axis; (c) for susceptibility for field parallel to *c* axis.

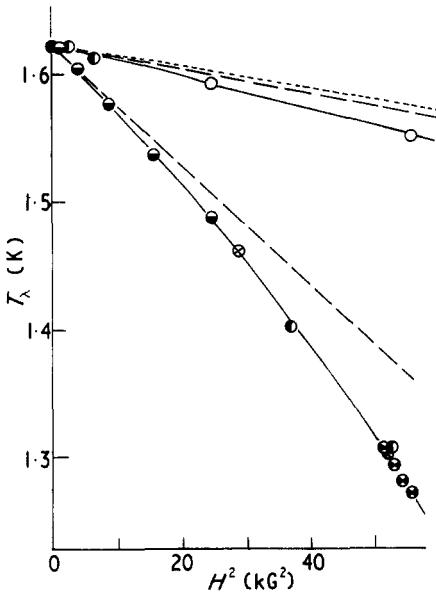


Figure 6. Dependence of Néel temperature of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ on field. \circ T_N for field parallel to *b* axis (Giauque *et al.*, from maxima in specific heat in field); \bullet T_N for field parallel to *c* axis (Giauque *et al.*, from maxima in specific heat in field); \otimes T_N for field parallel to *c* axis (McElearney *et al.*, from maxima in specific heat in field); \ominus T_N for field parallel to *c* axis (Giauque *et al.*, from maxima in $(\partial\chi/\partial T)_{P,H}$); \bullet T_N for field parallel to *c* axis (Gijsman *et al.*, from proton magnetic resonance). Broken curves: straight lines of slope equal to initial slope $\lim_{H \rightarrow 0} (\partial T_N / \partial (H^2))_P$ as predicted from magnetic Pippard plots of figure 5. Full curves: through experimental data cited.

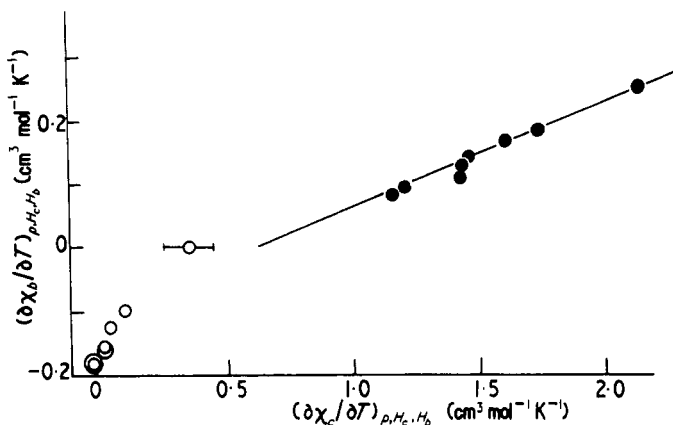


Figure 7. Plot for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ of corresponding values of the temperature coefficients of the susceptibilities for fields parallel to the b and c axes. Data as in figure 5.

If the slopes of the plots are used to estimate $(\partial T_\lambda/\partial(H^2))_p$ for fields parallel to the respective axes, there seems to be satisfactory agreement with the *initial* slope of plots (figure 6) of the observed values of T_λ at various fields. The increasing departures at higher fields seem to be due to curvature of a plot of T_λ against H^2 .

One further comparison which can be made arises as follows. The two Pippard's relations for the two susceptibilities, taken together, imply that

$$\left(\frac{\partial\chi_c}{\partial T}\right)_{p,H_c,H_b} \simeq \text{constant} + \frac{(\partial T_\lambda/\partial(H_c^2))_{p,H_b}}{(\partial T_\lambda/\partial(H_b^2))_{p,H_c}} \left(\frac{\partial\chi_b}{\partial T}\right)_{p,H_c,H_b}$$

A plot of the values of the temperature coefficient of χ_c against those of the temperature coefficient of χ_b (figure 7) is indeed linear for temperatures below T_λ .

4.2. Comments and comparisons with related investigations

Relation (3), discussed above and illustrated by data for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, is virtually equivalent to the relations discussed by Skalyo *et al* (1967), and stated by them to correspond to Fisher's (1962) microscopic analysis. The present discussion emphasizes the status of the relation as a *purely thermodynamic* result clearly indicating that, unless the slope of the graph is nearly zero (that is, unless T_λ is almost unaffected by changes in the magnetic field), a peak in C_{pH}/T will be accompanied by a peak in $|(\partial\chi/\partial T)_{p,H}|$, but not necessarily by a peak in χ itself. It is noteworthy, for example, that $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ exhibits associated peaks in C_p (Robinson and Friedberg 1960, Skalyo *et al* 1967) and $(\partial\chi/\partial T)_p$, in a range of temperature over which χ increases continually without passing through a maximum (Sawatzky and Bloom 1964).

Fisher's (1962) conclusion, from a statistical mechanical treatment of a very general kind, was that in the immediate vicinity of an antiferromagnetic Néel point the magnetic contribution to a specific heat is approximately proportional to $(\partial/\partial T)(\chi T)$. This was inferred first for a special case, and subsequently for increasingly general models (Sykes and Fisher 1958, 1962, Fisher 1959, 1960a, 1960b, 1962, and see also Wolf and Wyatt 1964 and Theumann 1970), which makes natural the possibility pointed out by Skalyo *et al* (1967) of correlation with purely thermodynamic results. However, if χ rises to a

maximum and then falls again, a purely thermodynamic analysis cannot distinguish whether the peak in C_{pH} will correspond to a temperature, below the maximum in χ , at which $(\partial\chi/\partial T)_{p,H}$ is large and positive, or to a temperature, above the maximum in χ , at which $(\partial\chi/\partial T)_{p,H}$ is large and negative. Fisher's treatment, in contrast, unambiguously points to the temperature *below* the maximum in χ .

Equation (3), just discussed, can be transcribed into a form relating to the magnetocaloric effect in the immediate vicinity of a λ transition. For the adiabatic magnetocaloric effect can be expressed in terms of the coefficient $(\partial T/\partial(H^2))_{s,p}$ which is equal to

$$-\frac{1}{2} \frac{T}{C_{pH}} \left(\frac{\partial\chi}{\partial T} \right)_{p,H}.$$

It then follows that in the vicinity of a λ transition marked by a sufficiently sharply rising maximum in C_{pH}/T :

$$\left(\frac{\partial T}{\partial(H^2)} \right)_{s,p} \simeq \frac{(\text{another}) \text{ constant}}{C_{pH}/T} + \left(\frac{\partial T_\lambda}{\partial(H^2)} \right)_p. \quad (7)$$

Thus, if the first term on the right may be neglected, then, for T very close to T_λ , $(\partial T_\lambda/\partial(H^2))_p$ should be approximately equal to the magnetocaloric coefficient $(\partial T/\partial(H^2))_{s,p}$ (cf Skalyo *et al* 1967).

Finally, equation (6) is very much akin to the equation inferred by Kornetzki (1935) for the dependence of a Curie temperature on hydrostatic pressure, on the basis of a certain approximation combining thermodynamic and molecular field approaches.

5. Dielectric Pippard's relations

For λ transitions accompanied by a very rapid dependence of dielectric properties on temperature, appropriate Pippard's relations are readily transcribed from the magnetic Pippard's relations given above. The form obtained in a direct transcription, however, gives relations in terms of the electric susceptibility referred to a given quantity of specimen; and *not* in terms of that referred to unit volume (the electric susceptibility most simply related to the dielectric constant, and so to the form in which data on dielectrics are customarily given).

Consider an isotropic dielectric. (Effects of anisotropy were treated by Janovec 1966.) By direct transcription from the magnetic case (replacing the magnetic field H by the electric field E), it is seen that, for sufficiently sharply rising peaks such that neighbouring contours of constant C_{pE}/T (etc) are approximately parallel, the following relations of approximate linearity hold in the immediate vicinity of a λ transition:

(i) A relation between C_{pE} and the dependence of the electric susceptibility on temperature

$$\left(\frac{\partial\chi}{\partial T} \right)_{p,E} \simeq \text{constant} - 2 \left(\frac{\partial T_\lambda}{\partial(E^2)} \right)_p \frac{C_{pE}}{T} \quad (8)$$

or (in terms of an electrocaloric coefficient)

$$\left(\frac{\partial T}{\partial(E^2)} \right)_{s,p} \simeq \frac{(\text{another}) \text{ constant}}{C_{pE}/T} + \left(\frac{\partial T_\lambda}{\partial(E^2)} \right)_p. \quad (9)$$

(ii) A relation between the dependence of the electric susceptibility on temperature and its dependence on the electric field

$$\left(\frac{\partial\chi}{\partial(E^2)}\right)_{T,p} \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial(E^2)}\right)_p \left(\frac{\partial\chi}{\partial T}\right)_{p,E}. \quad (10)$$

(iii) A relation between (isotropic) electrostriction and the coefficient of expansion α

$$\frac{1}{V} \left(\frac{\partial V}{\partial(E^2)}\right)_{T,p} \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial(E^2)}\right)_p \alpha. \quad (11)$$

(iv) A relation between (isotropic) electrostriction and the dependence of the electric susceptibility on temperature

$$\left(\frac{\partial\chi}{\partial T}\right)_{p,E} \simeq \text{constant} + \frac{2}{(\partial T_\lambda/\partial p)_E} \left(\frac{\partial V}{\partial(E^2)}\right)_{T,p} \quad (12)$$

(together with the ordinary Pippard's relations (1) and (2)). (p throughout denotes pressure, not electric polarization.)

In particular, it is important that a sharply rising peak in C_{pE}/T will be associated primarily with a corresponding peak in $|(\partial\chi/\partial T)_{p,E}|$, and not primarily with a peak in χ or in the dielectric constant. A maximum in the dielectric constant may well correspond to a temperature *above* T_λ .

5.1. Plots of actual experimental data

Plots of type (i) will be presented for two substances which exhibit a very marked variation of dielectric constant over a short range of temperature near T_λ . Ferroelectric transitions have already been examined by Janovec (1966) and Garland and Novotny (1969).

5.1.1. Solid hydrogen iodide. For solid hydrogen iodide there are two λ transitions, C_{pE} exhibiting a very sharply rising peak close to 70 K and a much less dramatic peak above 120 K.

For temperatures around the lower T_λ , there are available very complete and thorough measurements of the dielectric properties (Havriliak and Cole 1955, Cole and Havriliak 1957, Groenewegen and Cole 1967). The measurements of the specific heat (Giauque and Wiebe 1929), while of high quality, are unfortunately less complete than the dielectric data. No value of C_{pE} is reported for the interesting region 70 to 72 K (just above T_λ) in which, as T_λ is approached from above, $(\partial\epsilon/\partial T)_{p,E}$ and C_{pE}/T are *both* increasing. Consequently, no points can usefully be plotted for temperatures above T_λ . Further, the highest reported value of C_{pE} comes from a measurement in which the temperature rose by over 1 K.

In a plot of $(\partial\epsilon/\partial T)_{p,E}$ against C_{pE}/T for temperatures below T_λ (figure 8), quite good linearity obtains for 10 K below T_λ (save only for the largest C_{pE}/T , which, as indicated above, can only be an average value whose exact significance in the present context is rather suspect).

It is interesting and important that the maximum in C_{pE} , or that in C_{pE}/T , undeniably lies (i) at a lower temperature than that of the maximum in the dielectric constant, and (ii) very close to that of the maximum in the temperature coefficient of the dielectric constant (cf Fisher 1962).

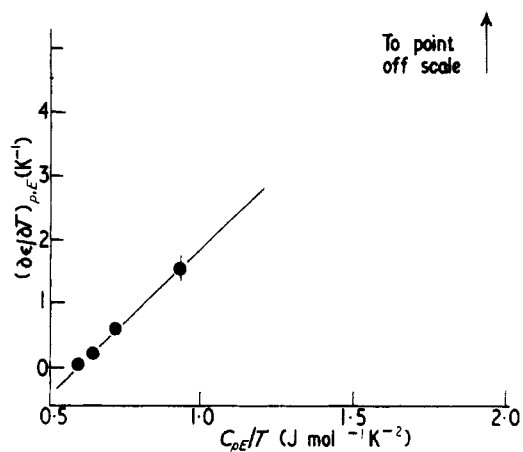


Figure 8. Solid hydrogen iodide. Corresponding values of $(\partial\epsilon/\partial T)_{p,E}$ and C_{pE}/T (for zero field) for temperatures below T_λ . (Range of temperature: 60 K to 70 K.)

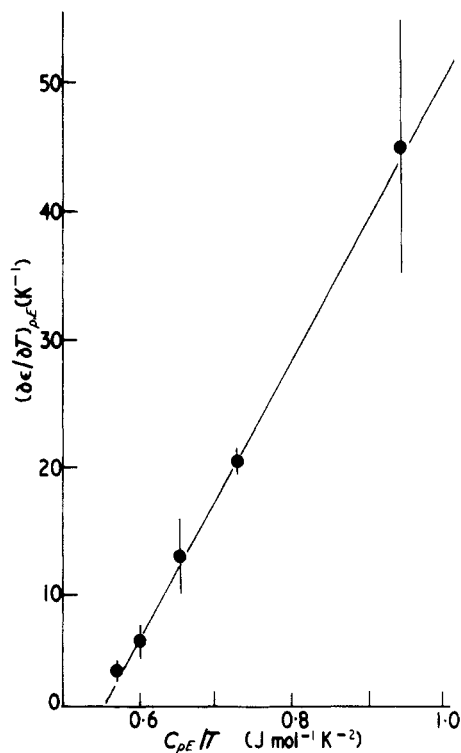


Figure 9. Solid hydrogen bromide. As for figure 8, but the temperatures tabulated by Brown and Cole (1953) for the dielectric data have been adjusted upwards by 0.6 K (see text). (Range of temperature: 84.6 K to 89.6 K.)

5.1.2. *Solid hydrogen bromide.* Solid hydrogen bromide exhibits three λ transitions, of which only that at the lowest temperature will be considered here. The other two exhibit much less dramatic (and less thoroughly demarcated) changes in the static dielectric

constant; and, further, between these two λ points the dielectric properties exhibit distinct thermal hysteresis.

The calorimetric specific heats (Giauque and Wiebe 1928) are of exceptionally high quality. Many of the values are based on very small rises in temperature, some as small as 0.02 K. The dielectric data (Brown and Cole 1953) unfortunately contain no value for a range of over 1 K below the temperature at which the static dielectric constant is a maximum; and this region, where the variation with temperature is greatest, would be of particular interest for the plots. Further, Brown and Cole reported that on slow warming the maximum appeared at a temperature up to 0.8 K higher than that at which it appeared on cooling; and that the temperature at which the maximum was attained was slightly different for two different pieces of apparatus.

With this as pretext, all of the temperatures tabulated by Brown and Cole have been adjusted upwards (by 0.6 K) so as to force their maximum in $|(\partial\epsilon/\partial T)_{p,E}|$ (just below that in ϵ) to coincide with the maximum found by Giauque and Wiebe in C_{pE} . When this is done, and a plot constructed on that basis (figure 9), very satisfactory linearity is obtained for a range of 5 K below T_λ . For temperatures just above T_λ , $(\partial\epsilon/\partial T)_{p,E}$ varies too rapidly for it to be possible to estimate it satisfactorily, and so no point is plotted.

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