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Revised thermodynamic relations for λ transitions in mixtures

II. Special relations for Curie points and Néel points

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Abstract. On the basis of the behaviour of magnetic and electric susceptibilities, and of magnetostriction and electrostriction, the possibility is investigated of obtaining additional Pippard's relations for the effect of change of composition on (magnetic or electric) Curie points and Néel points of mixtures.

The question is aired of whether further such relations might not sometimes be obtainable on the basis of the behaviour of properties other than equilibrium thermodynamic properties.

1. Introduction

Certain λ transitions are special in that they are associated with more or less drastic changes in magnetic properties (or analogous electrical properties). In consequence, for such λ transitions (Curie points and Néel points) there will be further thermodynamic relations additional to those (cf Rice 1954 and Pippard 1956 and 1957) relevant to all λ transitions.

Such λ transitions in mixtures are considered here.

2. Analysis in terms of magnetic properties, for mixtures not at temperatures at which they are ferromagnetic

The principal additional features for 'magnetic' λ transitions are (for isotropic materials not below their ferromagnetic Curie points, if any) more or less sharply-rising peaks (i) in $(\partial\chi/\partial T)_{p,H}$ (the temperature coefficient of the magnetic susceptibility referred to unit quantity of substance), and (ii) in the coefficient of magnetostriction $V^{-1}(\partial V/\partial(H^2))_{T,p}$.

For fixed p and H , these quantities are constant along contours (in the $x_B T$ plane) with slopes equal respectively to

$$(i) \quad - \frac{\partial^2 \chi}{\partial x_B \partial T} / \frac{\partial^2 \chi}{\partial T^2}$$

which is to be equated to

$$- \left(\begin{array}{l} \text{slope of graph of values of } (\partial\chi/\partial x_B)_{T,p,H}, \text{ for} \\ \text{various } T \text{ at fixed } p, H \text{ and } x_B, \text{ plotted against} \\ \text{corresponding values of } (\partial\chi/\partial T)_{p,H,x_B} \end{array} \right).$$

$$(ii) \quad - \frac{\partial^2 \ln V}{\partial x_B \partial (H^2)} \bigg/ \frac{\partial^2 \ln V}{\partial T \partial (H^2)}$$

which is to be equated to

$$- \left(\begin{array}{l} \text{slope of graph of values of } V^{-1}(\partial V/\partial x_B)_{T,p,H}, \text{ for} \\ \text{various } H \text{ at fixed } T, p \text{ and } x_B, \text{ plotted against cor-} \\ \text{responding values of the coefficient of expansion} \\ \alpha \equiv V^{-1}(\partial V/\partial T)_{p,H,x_B} \end{array} \right).$$

If the peaks at the λ transition rise sufficiently sharply, then the slope of the λ line ($\partial T_\lambda/\partial x_B$)_{p,H} approximates to the slope of neighbouring contours of constant ($\partial \chi/\partial T$)_{p,H,x_B} or to the slope of neighbouring contours of constant $V^{-1}(\partial V/\partial (H^2))$ _{T,p,x_B}. It therefore then approximates to the slopes of the graphs just prescribed.

If, further, these neighbouring contours are approximately parallel, then it follows that for a mixture anywhere in the vicinity of a Néel point:

(i) For various temperatures at fixed pressure, field, and composition

$$\left(\frac{\partial \chi}{\partial x_B} \right)_{T,p,H} \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_{p,H} \left(\frac{\partial \chi}{\partial T} \right)_{p,H,x_B}.$$

(ii) For various fields at fixed temperature, pressure, and composition:

$$\frac{1}{V} \left(\frac{\partial V}{\partial x_B} \right)_{T,p,H} \simeq \text{constant} - \left(\frac{\partial T_\lambda}{\partial x_B} \right)_{p,H} \alpha.$$

(The left hand side may be written in terms of partial molar volumes \tilde{V}_i as $(\tilde{V}_B - \tilde{V}_A)/V$, and so the relation is one between the effect of field on the partial molar volumes and the effect of field on the coefficient of expansion.)

These Pippard's relations apply only if the peaks rise sufficiently sharply, and the relevant contours are approximately parallel. When such is not the case, instead of approximate equalities there are only corresponding inequalities. (Compare the situation arising in the thermodynamic analysis, given in I, of the behaviour of properties exhibiting peaks in *all* λ transitions in mixtures.)

Moreover, the possibility of actual use of these relations is probably restricted to Néel points; there are difficulties in the attempted application of Pippard's relations to magnetic susceptibilities at temperatures just above a Curie point.

3. Corresponding situations for dielectric properties

For λ transitions associated with varying dielectric properties, an exactly similar analysis applies. The magnetic field H is throughout to be replaced by the electric field E , magnetic susceptibilities by electric susceptibilities, and magnetostriction by electrostriction. Curie points are now ferroelectric Curie points, and to Néel points there correspond temperatures at which an electric susceptibility varies with temperature the most rapidly.

4. Possibility of there being other special relations

The kind of analysis which leads up to the various Pippard's relations depends only on a certain quantity exhibiting a sufficiently dramatic peak. There is no need for the quantity in question to be an equilibrium thermodynamic property.

For any quantity Z such that $(\partial Z/\partial T)_{p,x_B}$ exhibits a suitable peak

$$\left(\frac{\partial T_\lambda}{\partial p}\right)_{x_B} \simeq \left(\begin{array}{l} \text{values of } (\partial T/\partial p)_{x_B, \partial Z/\partial T} \\ \text{at neighbouring points} \end{array}\right) = -\frac{\partial^2 Z/\partial p \partial T}{\partial^2 Z/\partial T^2}$$

$$= -\left(\begin{array}{l} \text{slope of graph of values of } (\partial Z/\partial p)_{T,x_B}, \text{ for} \\ \text{various } T \text{ near } T_\lambda, \text{ at fixed } p \text{ and } x_B, \\ \text{plotted against corresponding values of} \\ (\partial Z/\partial T)_{p,x_B} \end{array}\right)$$

and

$$\left(\frac{\partial T_\lambda}{\partial x_B}\right)_p \simeq \left(\begin{array}{l} \text{values of } (\partial T/\partial x_B)_{p, \partial Z/\partial T} \\ \text{at neighbouring points} \end{array}\right) = -\frac{\partial^2 Z/\partial x_B \partial T}{\partial^2 Z/\partial T^2}$$

$$= -\left(\begin{array}{l} \text{slope of graph of values of} \\ (\partial Z/\partial x_B)_{T,p}, \text{ for various } T \\ \text{near } T_\lambda, \text{ at fixed } p \text{ and } x_B, \\ \text{plotted against correspond-} \\ \text{ing values of } (\partial Z/\partial T)_{p,x_B} \end{array}\right).$$

The possibility must at least be envisaged that Z might sometimes be able to be taken not only as the entropy, the volume, or a (static) magnetic or electric susceptibility, but also perhaps as some such property as a viscosity, diffusion coefficient, refractive index, or dielectric or ultrasonic relaxation time (cf Garland and Novotny 1969).

References

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