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A SIMPLE THEORY OF THERMAL EFFECTS IN IONIC CRYSTALS

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ABSTRACT

An equation of state is obtained for ionic crystals based on the Born theory by assuming that the thermal motions of ions are uncorrelated and that the mean vibration energy of each ion is kT. The important feature of the theory is that the "thermal pressure" term is written entirely in terms of the interaction potentials. This is an advance over current Born theory equations of state which require a knowledge of the experimental coefficient of thermal expansion. The calculated volume thermal expansivities of the alkali halides at room temperature and atmospheric pressure are in good agreement with experiment (r.m.s. error 12·5%). For many purposes, the present theory appears to be an adequate approximation for ionic crystals at finite temperatures.

IN the Born theory of ionic crystals[1,2], the free energy per molecule of a crystal in the NaCl, CsCl or ZnS structures at 0° K is written as

$$G(r, P) = -\frac{ae^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + W_{rep}(r) + xPr^3 \qquad (1)$$

where r is the nearest neighbour distance, ae^2/r is the electrostatic interaction, C and D are the van der Waals dipole-dipole and dipole-quadrupole coefficients, $W_{rep}(r)$ is the repulsion energy, P is the pressure and xr^3 is the volume per molecule. The repulsion energy is usually written in the form[2]

$$W_{rep}(r) = n_1 h_{+-}(r) + \frac{n_2}{2}[h_{++}(R) + h_{--}(R)]\ ;$$
$$R = 2br \qquad (2)$$

where n_1 and n_2 are the numbers of first and second neighbours around an ion and $R(=2br)$ is the distance between second neighbours. h_{+-}, h_{++} and h_{--} are parametrised functions modelled differently in various approaches[2–4]. The equilibrium condition is given by

$$\left(\frac{\partial G}{\partial r}\right)_P = \frac{ae^2}{r^2} + \frac{6C}{r^7} + \frac{8D}{r^9} + n_1 h'_{+-}(r)$$
$$+ \frac{n_2}{2}[h'_{++}(R) + h'_{--}(R)] + 3xPr^2 = 0 \qquad (3)$$

where the primes denote derivatives with respect to r.

The Born theory is quite adequate to describe a number of static properties of ionic crystals and has many successes to its credit[2,5,6]. Its chief advantage is that calculations are relatively easy, making it both convenient and practical. Moreover, the present authors have developed in the recent past a formulation of the Born theory[3–10] which enables one to make *predictions* on the crystal properties of new compounds or new phases of existing compounds. Unfortunately, none of the versions of the Born theory developed so far can be used to compute thermal expansion coefficients or other related properties.

There *are* rigorous theories available to describe the anharmonic properties of crystals[11]. The calculations are however quite formidable and therefore not in the spirit of the Born theory. The usual approach is through the spectrum of lattice vibrations calculated by means of harmonic crystal dynamics. To calculate thermal expansion and other anharmonic properties, one either makes the quasi-harmonic approximation and calculates the variation of lattice frequencies with volume or carries through the full anharmonic theory. Neither approach lends itself to quick calculations.

Currently, Born theory calculations at finite temperatures are carried out by means of hybrid equations of state[2] such as those of Hildebrand[12] or Mie and Grüneisen[13]. In these approaches, the thermal effects are taken into account through a "thermal pressure" term which is written in terms of the *experimental* coefficients of thermal expansion. Such schemes which develop a theoretical description of a crystal only after experimental data are available are highly unsatisfactory. In principle, once the various crystal interactions are given, all crystal properties including the anharmonic thermal effects are implicitly described by them. One should therefore be able to calculate the "thermal pressure" term directly in terms of the interaction potentials. In this paper we present an extension of the Born theory which attempts to do this. To make the theory as simple as possible, we make certain approximations which are discussed below. At first sight these may appear to be rather drastic. A closer investigation however shows that the theory is physically quite well founded. This will be discussed in a later paper by Nityananda and Narayan[14].

In the present theory, we make the following simplifying approximations:

(*a*) We assume that the thermal motions of ions are totally uncorrelated. As we show below, this is equivalent to assuming that the ions vibrate in independent potential walls. Thus, in effect, we are replacing the complicated lattice spectrum by just two frequencies—one for each type of ion. In a later paper[14], an alternative simple theory is developed which seeks to include correlations also in an approximate way.

(*b*) The energy per mode of vibration is taken to be kT. We are thus working in the classical high temperature regime and also limiting ourselves to the quasiharmonic approximation. One could extend the theory to low temperatures in the quantum regime by developing an Einstein-like theory[15] for the two oscillators. This would be adequate at all except very low temperatures.

We begin by determining the average potential energy required to displace say a cation by a small amount (x_+, y_+, z_+). Taylor expansion of the various interactions retaining terms upto the second order shows that in general this depends on the displacements of the other ions also. However, because of the present approximation that the motions of ions are uncorrelated, all the cross-terms drop out on averaging and we can write the average potential energy of a displaced cation in the form

$$W_+(x_+, y_+, z_+) = 1/6\,[n_1 \nabla_r^2 h_{+-}(r) + n_2 \nabla_R^2 h_{++}(R)]\,(x_+^2 + y_+^2 + z_+^2) \tag{4}$$

$$\nabla_r^2 = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\,; \quad \nabla_R^2 = \frac{d^2}{dR^2} + \frac{2}{R}\frac{d}{dR} \tag{5}$$

where we have neglected the van der Waals interactions. The Coulomb term vanishes because $\nabla_r^2(1/r)$ is identically equal to zero. Thus, in the present approximation, we see that the ion moves in a potential well whose shape is independent of the displacements of the other ions. The spherically symmetric nature of the well is a consequence of the high symmetry of the structures which we are considering. By (4), all cations vibrate with a single frequency ν_+. So too the anions have one frequency ν_-. Thus, the present theory models the full lattice spectrum by means of just two frequencies.

From (4), equating the mean potential energy for displacements along each of x_+, y_+ and z_+ to $\frac{1}{2}kT$, we obtain

$$\overline{x_+^2} = \overline{y_+^2} = \overline{z_+^2} = \frac{3kT}{n_1 \nabla_r^2 h_{+-}(r) + n_2 \nabla_R^2 n_{++}(R)} \tag{6}$$

A similar expression can be written for the mean square displacements of the anions.

To obtain the equilibrium condition in the presence of thermal vibrations, we begin by rewriting the static equilibrium condition (3) in the following form

$$\frac{ae^2}{r^2} + \frac{6C}{r^7} + \frac{8D}{r^9} + n_1 \frac{d}{dr} h_{+-}(r) + \frac{2bn_2}{2}\left[\frac{d}{dR} h_{++}(R) + \frac{d}{dR} h_{--}(R)\right] + 3xPr^2 = 0. \tag{7}$$

The terms $dh_{+-}(r)/dr, dh_{++}(R)/dR$, etc., can be interpreted as repulsive forces directed along the corresponding bonds and equation (7) gives the condition for the overall equilibrium of all the forces of interaction. At finite temperatures, the various bond lengths fluctuate because of thermal vibrations of the ions. Thus, the repulsive force along a bond also fluctuates and this leads to an additional "rectified" component in the average repulsion per bond, proportional to the mean square fluctuation of the bond length. Including this effect, the equilibrium condition at finite temperatures becomes

$$\frac{ae^2}{r^2} + \frac{6C}{r^7} + \frac{8D}{r^9} + n_1\left[\frac{d}{dr} h_{+-}(r) + \frac{1}{2}(\overline{x_+^2} + \overline{x_-^2})\frac{d}{dr}\nabla_r^2 h_{+-}(r)\right] + \frac{2bn_2}{2}\left[\frac{d}{dR} h_{++}(R) + \overline{x_+^2}\frac{d}{dR}\nabla_R^2 h_{++}(R) + \frac{d}{dR} h_{--}(R) + \overline{x_-^2}\frac{d}{dR}\nabla_R^2 h_{--}(R)\right] + 3xPr^2 = 0. \tag{8}$$

Equation (8) is an *equation of state* for simple ionic crystals. The extra terms over those in (7) are the contributions from "thermal pressure". As in the 0° K case, (8) requires solving only one transcendental equation.

Using equation (8) we have calculated the volume thermal expansivities β of the alkali halides at room temperature and atmospheric pressure. For $h_{+-}(r)$, $h_{++}(R)$ and $h_{--}(R)$, we have employed our compressible ion potentials[3,4]*. The r.m.s. error in the calculated values of β (Table I) is only 12·5%. A more detailed investigation[14] seems to suggest that most of the errors arise from the use of inadequate

* However, it should be noted that the theory developed here can be used with any version of the Born theory.

TABLE I

Experimental and theoretical thermal expansivities β (in 10^{-4} per °K) of the alkali halides

Crystal	β_{exp}	β_{calc}	Error (%)	Crystal	β_{exp}	β_{calc}	Error (%)
LiF	0·92	0·90	− 1·8	KBr	1·10	1·24	12·3
LiCl	1·22	1·15	− 6·1	KI	1·25	1·33	6·1
LiBr	1·40	1·25	−10·7	RbF	0·95	1·06	11·6
LiI	1·67	1·44	−13·8	RbCl	0·99	1·21	23·2
NaF	0·98	1·01	2·7	RbBr	1·04	1·28	23·1
NaCl	1·10	1·15	4·8	RbI	1·19	1·28	7·8
NaBr	1·19	1·18	− 0·8	CsF	0·95	0·98	3·1
NaI	1·35	1·35	0·1	CsCl	1·37	1·18	−13·5
KF	1·00	1·10	10·2	CsBr	1·39	1·19	−14·4
KCl	1·01	1·22	20·6	CsI	1·46	1·18	−19·4

r.m.s. error = 12·5%.

interaction potentials rather than from oversimplifications in the theoretical model. We therefore believe that the present theory is adequate for many purposes.

There are many situations where one would like to have estimates of the properties of real or hypothetical crystals without having to do the experiments. The present theory could be used to calculate approximate thermal expansion coefficients of cubic ionic crystals within an r.m.s. error of about 15%. However, although we have discussed only thermal expansion in this paper, the theory has a wider applicability. We have in (8) an *equation of state* for simple ionic crystals. This has already been of use in a theory[16] which we have developed to explain the electronic transitions in the samarium chalcogenides. Moreover, we can write an approximate *free energy* for the crystal at finite temperatures in terms of the Einstein oscillators of frequencies ν_+ and ν_-. This would be of use in calculating specific heats and also in studying phase boundaries at finite temperatures.

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