Thermal Properties of Alcaline-Earth-Oxides

III. Analysis of Anharmonic Effects

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Experimental heat capacity data for the alcaline-earth-oxides have been used to analyse by a new method the high temperature thermodynamic properties of these crystals in terms of quasi-harmonic and explicit anharmonic contributions.

The explicit anharmonic contribution ΔC is consistent with theoretical predictions; ΔC is proportional to T in a first order approximation. The factor of anharmonicity A is negative for MgO, $A = (-0.4 \pm 0.4) \cdot 10^{-5}$ K^{-1}, for SrO $A = (-2.8 \pm 1) \cdot 10^{-5}$ K^{-1} and for BaO $A = (-3.9 \pm 1) \cdot 10^{-5}$ K^{-1}, but positive for CaO $A = (2.3 \pm 1.2) \cdot 10^{-5}$ K^{-1}.

Comparison with the results of analysis of the anharmonic effects in the alcaline-halides shows that the alcaline-earth-oxides may be treated by the same models valuable for the alcaline-halides. The results suggest that the type of anharmonic forces is determined in the alcaline-halides as well as in the alcaline-earth-oxides primarily by the cation of the salt.

I. Introduction

In recent years TOSI and FUMI[1], MARTIN[2], NEWSHAM[3], OVERTON[4], LEADBETTER et al.[5] and others have used the experimental results of the specific heat measurements in the high and low temperature range to analyse the thermodynamic functions of several substances in terms of the quasi-harmonic and explicit anharmonic contributions. From these analyses the theory seems well established, and many anharmonic effects have been explained, and when the experimental accuracy was good enough conclusions could be drawn about the anharmonic forces in the solid.

However, the accuracy of such informations is generally limited because a correction is necessary in order to reduce the high temperature experimental specific heat data to a fixed volume (i. e. absolute zero) requiring parameters as density ϱ, elastic constants c_{ij}, coefficient of dilatation α and compressibility χ as well as the variation with temperature and volume. But it is very difficult to find a substance of which all required values are known. Even methods which can be applied within the range of room temperature and lower have serious disadvantages. The quasiharmonic region had to be corrected for explicit anharmonic effects. The anharmonic contributions must be derived by an iterative analysis.

Recently VIEIRA and HORTAL[6] proposed a method of deriving the anharmonic coefficients from experimental data at intermediate temperatures only that does not involve successive approximations. This method has been used successfully for analysing the anharmonic contributions of KF.

It was pointed out in the preceding papers[7] that an appreciable positive anharmonic contribution to the specific heat is present for all alcaline-earth-oxides. Unfortunately, due to the lack of accurate experimental data for the above indicated parameters it did not seem reasonable to analyse the anharmonic effects with the known methods.

The analysis given in this paper starts from the new method of VIEIRA and HORTAL[6] using experimental specific heat values, published in Part I.

II. Theory

1. General

The essential problem is to separate the quasi-harmonic and the explicit anharmonic contribution

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of the measured specific heat data. If the anharmonicity is small enough to be treated as a perturbation, the free energy F of the solid may be written as:

$$F(T,V)=F^{\mathrm{qh}}(T,V)+\Delta F^{\mathrm{anh}}(T,V) \qquad (1)$$

where F^{qh} is the quasiharmonic contribution and ΔF^{anh} represents the explicit anharmonic contribution. But it is more useful to study the isochronic specific heat c_{V} or the entropy S, which must contain the same information about the lattice vibrations. The entropy S is more convenient since it is obtained directly from the isobaric specific heat c_p, which is a well measurable quantity. Therefore we analyse $S(T,V)$ basically in terms of the equation:

$$S(T,V)=S^{\mathrm{qh}}(T,V)+\Delta S^{\mathrm{anh}}(T,V). \qquad (2)$$

To study the explicit anharmonic contribution, the total anharmonicity had to be corrected for the contribution due to the thermal expansion of the lattice aloe, which represents generally the main part. This is done by reducing the equivalent Debye-temperature to a fixed volume, which usually is chosen to be the 0 K volume V_0.

Then the quasiharmonic contribution is obtained by fitting the $S^{\mathrm{qh}}(V_0,T)$ values inside a convenable range of temperatures to the SALTER expansion[8]:

$$S^{\mathrm{qh}}(V_0,T)=3\,N\,K\Big[-\ln\frac{\Theta(0)}{T}+\frac{4}{3} - \sum_{n=1}(-1)^n\,\frac{B_{2n}}{(2\,n)!}\,\frac{2\,n-1}{2\,n}\cdot\frac{3}{2\,n+3}\left(\frac{\Theta(2)}{T}\right)^{2n}\Big] \qquad (3)$$

where B_{2n} are the Bernouilli numbers. The corresponding expansion for the Debye equivalent temperature is given by

$$\Theta_{\mathrm{S}}^{\mathrm{qh}}\,(V_0,T)=\Theta(0)\left(1+\sum_{n=1}^{\infty}a_n\,T^{-2n}\right) \qquad (4)$$

where $\Theta_{\mathrm{S}}^{\mathrm{qh}}$ is the "quasiharmonic Debye temperature" and $\Theta(0)$ and a_n are characteristic constants related to the moments of the frequency spectrum. But it must be recognized that an appreciable anharmonicity must be present down to the lowest temperatures[9]. Therefore the entropy cannot be defined as a true harmonic entropy, rather than an apparent quasiharmonic entropy *. For most solids at low temperatures these anharmonic effects are quite small; therefore the apparent quasiharmonic entropy agrees quite well with the true harmonic entropy.

2. Method of Analyzing the Results (Theory of Vieira and Hortal)

The first step to obtain the explicit anharmonic contribution to the entropy is the reduction of the equivalent Debye temperature to the volume at 0 K. This is done by the following formula[10]

$$\Theta(V_0,T)/\Theta(V_{\mathrm{T}},T)=(\varrho_0/\varrho_{\mathrm{T}})^{\gamma(0)} \qquad (5)$$

where $\gamma(0)$ is an appropriate Grüneisen-parameter, which coincides with the high temperature limit of the Grüneisen function $\gamma(T,V)$.

For a cubic crystal if the density ϱ as a function of temperature is not known, relation (5) may be replaced by:

$$\frac{\Theta(V_0,T)}{\Theta(V_{\mathrm{T}},T)}=\left[1+\int_0^T\alpha\,\mathrm{d}T\right]^{\gamma(0)}$$

or in first order approximation:

$$\frac{\Theta(V_0,T)}{\Theta(V_{\mathrm{T}},T)}\cong 1+\gamma(0)\int_0^T\frac{c_p\,\chi_{\mathrm{S}}\,\gamma}{V}\,\mathrm{d}T$$

where α is the dilatation coefficient and χ_{S} the adiabatic compressibility. Considering that the Grüneisen function and the coefficient χ_{S}/V are nearly constant down to the low temperature region, the last expression can be approximated by:

$$\frac{\Theta(V_0,T)}{\Theta(V_{\mathrm{T}},T)}\cong 1+\gamma(0)^2\,\frac{\chi_{\mathrm{S}}}{V}\int_0^T c_p\,\mathrm{d}T \qquad (6)$$

which can be calculated easily.

The next step to compute the explicit anharmonic contribution is the good fitting of the experimental results of the specific heat measurements to the quasiharmonic expansion, represented by Eq. (3) in spite of the presence of anharmonic contributions at low temperatures due to zero point energy. The region where the experimental results agree with the quasiharmonic expansion is called by VIEIRA and HORTAL[6] "apparent quasiharmonic region". The apparent quasiharmonic range values are described by introducing perturbations $\delta\Theta(2\,n)$ to the coefficients of expansion in formula (3):

$$S^{\mathrm{exp}}(V_0,T)=3\,N\,K\Big[-\ln\frac{\Theta(0)+\delta\Theta(0)}{T}+\frac{4}{3} - \sum_{n=1}^{\infty}(-1)^n\,\frac{B_{2n}}{(2\,n)!} \times\frac{2\,n-1}{2\,n}\cdot\frac{3}{2\,n+3}\cdot\left(\frac{\Theta(2\,n)+\delta\Theta(2\,n)}{T}\right)^{2n}\Big]. \qquad (7)$$

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* Or also called "effective entropy"[9].

These perturbations are due to the anharmonicity within the apparent quasiharmonic region. Now the explicit anharmonic contribution of the entropy can be divided in two parts:

$$\Delta S^{\text{anh}}(V_0, T) = \Delta S^{\text{anh}}_{\text{exp}}(V_0, T) + \Delta S^{\text{anh}}_{\text{extr}}(V_0, T) \quad (8)$$

where ΔS^{anh} is the explicit anharmonic contribution to the entropy; this means the difference between the experimental value corrected to fixed volume and the corresponding quasiharmonic value,

$\Delta S^{\text{anh}}_{\text{exp}}(V_0, T)$ is the anharmonic contribution relative to the extrapolation of the apparent quasiharmonic range which means the difference between the experimental values and the extrapolated values using Equation (7).

$\Delta S^{\text{anh}}_{\text{extr}}(V_0, T)$ finally is the difference between the experimental values of the apparent quasiharmonic region and the quasiharmonic ones.

Obviously, in the apparent quasiharmonic range

$$\Delta S^{\text{anh}}(V_0, T) = \Delta S^{\text{anh}}_{\text{extr}}(V_0, T).$$

Following the concept of BARRON[9], the anharmonic properties of a crystal are given to a first order approximation by an effective frequency-distribution, which changes with temperature. Usually, the deviation of the effective frequency spectrum from the harmonic spectrum is described by temperature dependent frequency-shifts $\delta\nu_j$ for each normal mode j. The "shifts" leading to the effective spectra of the entropy S and the free energy F are given by $\delta{\nu_j}^S$ and $\delta{\nu_j}^F$, respectively.

To a first order approximation the anharmonic contributions normaly are sums of a cubic (3) and a quartic (4) potential energy-term. Therefore the total shift $\delta\nu_j$ can be separated into two contributions:

$$\delta\nu_j = \delta\nu_{j(3)} + \delta\nu_{j(4)}\,.$$

BARRON[9] has shown that

$$\delta\nu^S_{(4)} = \delta\nu^N_{(4)} = 2\,\delta\nu^F_{(4)} \quad \text{and} \quad \delta\nu^S_{(3)} = \delta\nu^N_{(3)}\,,$$

where the index "N" indicates the shifts calculated by MARADUDIN and FEIN[12]. Furthermore, OVERTON[4, 13] demonstrated that $\delta\nu^N_{(3)} = 2\,\delta\nu^F_{(3)}$. This yields:

$$\delta{\nu_j}^S = \delta{\nu_j}^N = 2\,\delta{\nu_j}^F. \quad (9)$$

Starting from this relation a very useful equation for the frequency-shift may be derived[14].

When the frequency of a normal mode is changed from ν^{harm} to $\nu^{\text{harm}} + \delta\nu^S$ the corresponding changes in its contribution to F and S may be written to a first order by:

$$\delta f = (\partial F/\partial\nu)_T\,\delta\nu^F; \quad \delta S = (\partial S/\partial\nu)_T\,\delta\nu^S; \quad (10\,\text{a, b})$$

δF and δS are connected by:

$$\delta S = -\mathrm{d}\,\delta F(V_0, T)/\mathrm{d}T. \quad (11)$$

Equations (10) and (11) together yield:

$$\delta S = -\left[\frac{c}{\nu}\,\delta\nu^F + \frac{e}{\nu}\,\frac{\mathrm{d}\nu^F}{\mathrm{d}T}\right]. \quad (12)$$

Here c and e denote the contribution of one mode to the specific heat at constant volume and to the vibration energy.

Substitution of (10 b) in (12) gives:

$$\delta\nu^S - \delta\nu^F = (e/c)\,\mathrm{d}\nu^F/\mathrm{d}T\,. \quad (13)$$

Taking into account that $\delta\nu^F/\mathrm{d}T = \mathrm{d}\,\delta\nu^F/\mathrm{d}T$ and that $\delta\nu^S = 2\,\delta\nu^F$ [Eq. (9)] relation (13) becomes:

$$\delta\nu^S = (e/c)\,\mathrm{d}\,\delta\nu^S/\mathrm{d}T$$

and with $c(V_0, T) = \mathrm{d}e(V_0, T)/\mathrm{d}T$:

$$\mathrm{d}\ln\delta\nu^S/\mathrm{d}T = \mathrm{d}\ln e/\mathrm{d}T$$

and by integration:

$$\frac{\delta{\nu_j}^S(V_0, T)}{\nu_j} = \frac{\delta{\nu_j}^S(V_0, 0)}{\nu_j\,e_z(V_0, 0)}\,e_j(V_0, T) = b_j\,e_j(V_0, T) \quad (14)$$

where b_j is a characteristic constant for each normal frequency mode. The relative frequency shift is proportional to the energy e_j of the mode.

The anharmonic contribution to the entropy can be expressed in first order by

$$\Delta S^{\text{anh}}(V_0, T) = -\sum_{j=1}^{3N} c_j\,\frac{\delta{\nu_j}^S}{{\nu_j}^S} = -\sum_{i=1}^{3N} c_j\,b_j\,e_j\,. \quad (15)$$

Assuming that approximatively all the b_j are the same, $b_j = 3\,N\,B$, where B is a characteristic constant of the crystal and that $3\,N\sum_{j=1}^{3N} c_j\,e_j = E_V\,C_V$, we obtain the expression used in Ref.[6]

$$\begin{aligned}\Delta S^{\text{anh}}(V_0, T) &= -B\,E_V\,C_V \\ &= A\,(E_V\,C_V/3\,N\,K). \quad (16)\end{aligned}$$

From Eqs. (3), (7) and (8) $\Delta S^{\text{anh}}_{\text{exp}}$ is obtained:

$$\frac{\Delta S^{\text{anh}}_{\text{extr}}(V_0, T)}{3\,N\,K} = -\frac{\delta\Theta(0)}{\Theta(0)} + \sum_{n=1}^{\infty}\left(\frac{b_{2n}}{T}\right)^{2n} \quad (17)$$

where b_{2n} are polynomials of $\Theta(2n)$ and $\delta\Theta(2n)$.

In the apparent quasiharmonic region where $T<T''$, Eqs. (16) and (17) must be equivalent, therefore:

$$E_V C_V = \frac{(3NK)^2}{A}\left[-\frac{\delta\Theta(0)}{\Theta(0)} + \sum_{n=1}^{\infty}\left(\frac{b_{2n}}{T}\right)^{2n}\right]. \quad (18)$$

The values of $E_V C_V$ obtained by the expansion (18) for $T>T''$ are called $(E_V C_V)_{\text{extr}}$.

Now from relations (8), (15), (17) and (18) the following expression is easily obtained:

$$A = 3NK\, \Delta S_{\text{exp}}^{\text{anh}}(V_0, T)/[E_V C_V - (E_V C_V)_{\text{extr}}]. \quad (19)$$

From this very simple relation the anharmonic coefficient A can be calculated without using an iterative method.

For relatively high temperatures, knowing that $(E_V C_V)/(3NK)^2 = T$ and defining

$$T' = \lim_{T\to\infty} \frac{(E_V C_V)_{\text{extr}}}{(3NK)^2} \quad (20)$$

relation (19) yields:

$$\Delta S_{\text{exp}}^{\text{anh}}/3NK = A(T-T').$$

By simple mathematical transformations $\delta\Theta(0)$ and $\delta\Theta_z(0)$ are deduced[6]:

$$\delta\Theta(0) = -AT'\,\Theta(0), \quad (21)$$

$$\delta\Theta_z(0) = A(E_z/3NK)\,\Theta(0) \cong -A\tfrac{3}{8}\Theta(2)\,\Theta(0), \quad (22)$$

$$E_z = \tfrac{9}{8}NK\,\Theta(1) \cong \tfrac{9}{8}NK\,\Theta(2). \quad (23)$$

III. Results of Data Analysis

1. Experimental Values

Our starting point is to collect and to select the experimental data required in the analysis of the anharmonic effects.

The experimental specific heat values are those presented in Part I[7]. The following Table 1 indicates some known quantities for the density ϱ, the adiabatic and isothermal compressibilities χ_S and χ_T, the dilatation coefficient α and the Grüneisen parameter γ.

Table 1. Density, adiabatic and isothermal compressibility and dilatation coefficient. Data are at room temperature unless otherwise indicated.

	MgO	CaO	OSr	BaO
ϱ [g/cm^3]	3.58[5]	3.295[16]	5.008[17]	5.72[18]
χ_S [cm^2/dyn] 10^{12}	0.645[19]	0.92[20]	1.08[21]	—
χ_T [cm^2/dyn] $\cdot 10^{12}$	0.59[22]	0.88[22]	0.83[22]	1.74[22]
α (K)$^{-1}$ 10^5	2.9[23]	2.8[24]	9.75[25]	5.34[25 a]
γ	1.5	1.24	1.22	1.21

[a] Extrapolated from 890 K.

The data used will now be considered in some more detail for each oxide:

MgO: Accurate and extensive data which are in rather good agreement already exist for MgO. The high temperature limit of the $\gamma(T, V)$ function has been calculated by GANESAN[23]. It is $\gamma(0) = 1.5$.

CaO: The values reported in the literature for CaO are also quite consistent and sufficiently precise. The values of γ have been given in Ref. [24]; $\gamma = 1.24$.

SrO: The mean dilatation coefficient $\alpha = 9.75 \times 10^{-5}$ K^{-1} ** given by EISENSTEIN[25] for SrO is unusually high, compared with the equivalent mean values for the other alcaline-earth-oxides[26, 27]. Using this value of α, corrected by extrapolation to 293 K the calculated value for the Grüneisen parameter is $\gamma = 3.5$. This result differs considerably from usually known data. It seems reasonable, taking into account the similarity of the variation of the different physical properties of the alcaline-earth-oxides (see Part II), that the dilatation coefficient α as well as the Grüneisen parameter γ should vary smoothly between MgO and BaO in the same manner as for the alcaline-halides. In these compounds γ decreases smoothly with increasing mass of the cation. Therefore the applicability of the data of α of EISENSTEIN[14] for SrO is doubtful and there seems to be no reason why γ(SrO) should not be included in the range between γ(BaO) and γ(CaO). Therefore we suppose the Grüneisen parameter of SrO equal to $\gamma(\text{SrO}) = 1.22$. Nevertheless, the following calculations shall show that the incertainty of γ does not affect essentially the informations about the anharmonicity which we may derive from the calculations.

BaO: To our knowledge, the mean value of α, obtained by EISENSTEIN[25] is the only one available at present. This data has been extrapolated to 293 K assuming that the temperature variation of the mean dilatation coefficient of BaO may be represented by the temperature variation of α of MgO[26] and CaO[27]; the resultant value is $\alpha = 3.7 \times 10^{-5}$ K^{-1}. We have obtained a value of $\gamma = 1.21$.

** For the range 330–1250 K.

2. *Correction to Fixed Volume*

Next step is to calculate the entropy $S(T, V)$ from the experimental C_p-data and then the Debye temperature Θ^S is taken from the tables of Giguere and Boisvert[28]. The correction to the volume at 0 K is computed using Equation (6). For MgO directly formula (5) is used with

$$\varrho_T = \varrho_0 [1 - T\,D(\Theta^w/T)] \qquad (24)$$

because the variation of the density ϱ_T as function of temperature is well known. The three parameters ϱ_0, a, Θ^w have been calculated by fitting the experimental ϱ_T-data[15] to relation (24):

$$\varrho_0 = 3.592\ \text{g/cm}^3;\quad a = 3.66 \cdot 10^{-5}\ \text{K}^{-1};\quad \Theta^w = 654\ \text{K}.$$

Only for MgO the correction can be carried out directly by formula (5). For the other oxides the temperature variation of the densities are not established with any great certainty, so that we had to calculate the correction using the first order approximation, given by Equation (6). For MgO both expressions (5) and (6) were applicated. The results for $\Theta(V_0, T)/\Theta(V_T, T)$ differ by less than 0.02% at 320 K. Therefore the correction is thought to be quite accurate also for CaO, SrO and BaO. It should be noted that a variation of γ of SrO by 0.1 results in changing the rapport $\Theta(V_0, T)/\Theta(V_T, T)$ by 0.06% only at 322 K.

3. *Quasiharmonic Region; Zero Point Energy*

In Figs. 1 – 4 we have represented $\Theta_D^S(V_0, T)$ vs. $1/T^2$. The Θ_D^S data have been fitted by a least square method to the quasiharmonic expansion according to Equation (4). For each data set analysed the number of coefficients in the expression and the range of temperature was varied. We have followed the same criterium as Ref. [6] to select the best fit. From the coefficients of the expansion the characteristic temperatures $\Theta(2n)$ are computed based on the equations given by Tosi and Fumi[1]. The values of $\Theta(2n)$ obtained are given in Table 2.

Table 2. Characteristic temperatures $\Theta(2n)$.

(in K)	MgO	CaO	SrO	BaO
Θ (0)	765.7 ± 3	580.2 ± 3	392.5 ± 1	276.7 ± 0.7
Θ (2)	777 ± 15	601 ± 10	431.5 ± 4	344 ± 2
Θ (4)	788 ± 35	616 ± 20	451 ± 10	371 ± 7
Θ (6)	—	—	460 ± 20	378 ± 15

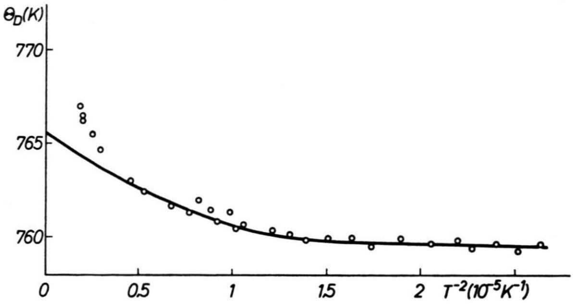

Fig. 1.

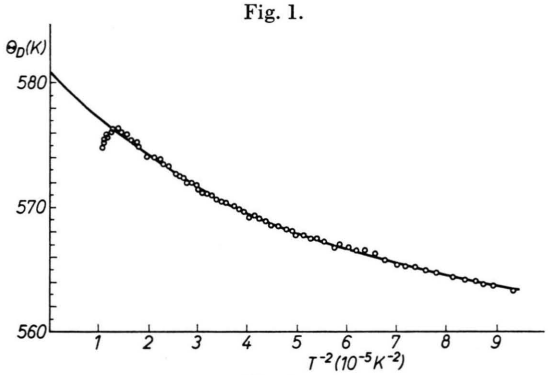

Fig. 2.

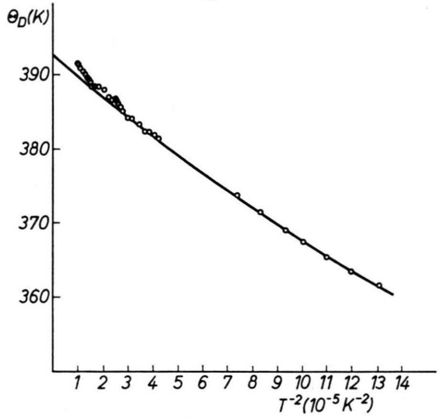

Fig. 3.

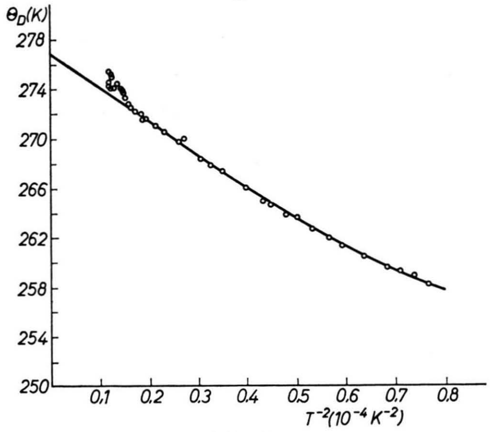

Fig. 4.

The results for the coefficients $\Theta(2n)$ were converted to E_z, using relation (23). The calculated values are given in Table 3. The results for E_z overlap those deduced in Part II from the analysis of the specific heat at constant volume. For MgO the agreement with the results of BARRON et al.[29] is very good.

4. *Calculation of A, T', $\delta\Theta(0)$, $\delta\Theta_z(0)$*

The calculations of these characteristic parameters of the leading anharmonic contribution of the entropy are performed by use of relations (19) to (22). We obtain A by use of expression (19):

- $\Delta S_{\text{exp}}^{\text{anh}}$ is directly deduced from the difference between the experimental data and the extrapolated values using Equation (7).
- The fitting of $E_V C_V$ within the apparent quasiharmonic region has been done following the same method as for Θ_{qh}^S. To find the best fit, the same criterium was applicated.

The computed ranges are $180 < T < 280$, $120 < T < 250$, $80 < T < 210$ K and $53 < T < 253$ K for MgO, CaO, SrO and BaO. The calculation of A for MgO has been performed using also specific heat data above 300 K, given by DOUGLAS and VICTOR[30].

The results are shown in Table 3. The values are mean values at several temperatures. The estimated standard deviation of the values of A is smaller than 10^{-6} K^{-1} for the 4 substances. The uncertainty of A, includes the errors of the experimental data.

The independent term of the $E_V C_V$ expansion[17] enables us to deduce T' [Eq. (20)]; the calculated values are indicated also in Table 3.

Finally, using the relations (21) and (22), the numerical values for $\delta\Theta(0)$ and $\delta\Theta_z(0)$ for the alcaline-earth-oxides have been obtained (Table 3).

IV. Discussion

The anharmonic contributions for the different alcaline-earth-oxides and alcaline-halides are best compared as function of the values $A\,\Theta(2)$, given in Tables 3 and 4. For the oxides the values of $A\,\Theta(2)$ are negative except for the value for CaO. The data for MgO appears to be significantly smaller than those for the other oxides. The tables show also that the explicit relative anharmonic contribution $A\,\Theta(2)$ is larger for CaO, SrO and BaO than for any other ionic crystals investigated so far (with the exception of CsBr).

No theoretical calculations on realistic models of anharmonic effects of the alcaline-earth-oxides have been performed yet. But some calculations have been done for cubic and hexagonal structures[31, 32]. The approximations appear generally to be in good quantitative agreement. WALLACE[32] derived a general expression for the high temperature contribution to the anharmonic free energy at constant volume for the case of a f.c.c. lattice with two atoms per unit cell. The cubic and quartic potential-energy-terms are derived by calculation of the two body central forces interactions with various ranges

Table 3. Zero point energy, anharmonic coefficient, perturbation $\delta\Theta$ for the alcaline-earth-oxides.

	MgO	CaO	SrO	BaO
E_z(J/Mol)[a]	14700 ± 300	11200 ± 400	8050 ± 250	6250 ± 220
E_z(J/Mol)[b]	14450 ± 100	11430 ± 100	7760 ± 80	6340 ± 60
A(K^{-1})10^5	− 0.4 ± 0.4	+ 2.3 ± 1.8	− 2.8 ± 1	− 3.9 ± 1
T' (K)	365	309	247	217
$\delta\Theta$(o) (K)	1.2	− 4.2	+ 2.7	+ 2.4
$\delta\Theta_z$(o) (K)	0.9	− 3.1	+ 1.8	+ 1.4
$(\delta\Theta\text{o})/\delta\Theta_z(\text{o})$	1.3	1.4	1.5	1.7
$A\Theta(2)\cdot 10^2$	− 0.3	+ 1.4	− 1.2	− 1.3

[a] Calculated in Part II.

[b] Calculated by formula (22), with $\Theta(0)$ obtained form interpolation of $\Theta(2n)$ values.

Table 4.

	KF[4]	KCl[33]	KBr[33]	KJ[1]	NaCl[33]	NaJ[1]	CsBr[34]	CsI[34]
A(K^{-1}) 10^4	− 2.1	+ 2.8	+ 3.5	+ 0.5	− 1.5	− 0.2	− 11.4	− 9
$A\Theta(2)\cdot 10^2$	− 0.69	+ 0.66	+ 0.65	+ 0.08	− 0.33	− 0.04	− 1.5	− 0.9

of the forces, represented by a Lennard-Jones potential. The leading anharmonic contribution to the specific heat at constant volume is given by

$$\Delta C_V^{\mathrm{anh}} = -(2/T)\,(F_{3T}+F_{4T}).$$

For the Lennard-Jones models F_{3T} is always negative and fairly insensitive to the range of forces, but F_{4T} is always positive and increases markedly with decreasing range of forces. ΔC_V is negative, but becomes quite small as the range of forces increases. Therefore the magnitude of the anharmonic contribution is determined by a balance of contributions of opposite sign arising from the asymmetric cubic term and the symmetric quartic term in the lattice potential energy. So the factor $A\,\Theta(2)$ is for different crystals a relative measure of the balance of terms of the lattice potential energy, depending upon the detailed nature of the interatomic forces.

Experimental results[5] of A for the alcaline-halides suggest that the relative importance of the cubic term decreases as the coordination number increases.

Furthermore, it seems that the type of anharmonic forces, this means whether the cubic or the quartic term dominates, depends primarily on the cation of the salt[33].

Looking for the factor $A\,\Theta(2)$ in a series of alcaline-halides, having the same cation, this value decreases with increasing diameter of the anion. The interatomic interaction between the cations themselves is shielded by the electron clouds of the larger anions; F_{4T}, which depends critically on the range of forces, decreases.

It appears likely that for open structures like the potassium-halides (with the exception of KF) and CaO large positive anharmonic contributions will be found. These compounds show also some other anomalous physical properties such as relatively low density and relatively high compressibility, compared with the other halides and oxides. WEIR[22] has drawn attention to the fact that probably the unusually open electronic structure of the compounds of the isoelectronic ions Ca and K is responsible for their unusual physical properties. We think that the positive sign of the anharmonicity is a further characteristic property of these substances.

An exception is KF, which has a relatively large cation anion mass ratio. This is the reason why the above mentioned shielding effect is small in KF; the quartic term dominates the cubic term and A becomes negative.

The same arguments hold for the other substances. In SrO and BaO, the shielding of the cations by the smaller anions is quite small. A large negative anharmonicity is observed. Contrarily, in MgO the shielding is much more important. Here the cubic term F_{3T} compensates the quartic term from which only a small anharmonicity results.

CaO, which has a large positive anharmonicity is similar to the potassium-halides. The term F_{3T} dominates the term F_{4T}, while for the other oxides the quartic term was dominant. CaO has also a relatively open structure with a low density and a large compressibility, compared with SrO, BaO and MgO.

V. Conclusion

The analysis of high temperature thermodynamic data in terms of quasiharmonic and explicit anharmonic contribution have been applied to the alcaline-earth-oxides. The explicit anharmonic contribution ΔC has the theoretically expected temperature dependence: ΔC is proportional to T. With exception of CaO, the factor of anharmonicity A is negative.

The conclusions of the theoretical work of WALLACE[32] have been used qualitatively to analyse the experimental data. Comparison between the alcaline-halides and oxides show that the magnitude and sign of anharmonicity are mainly influenced by the cation of the compounds. A very interesting feature is the similar behaviour of the isoelectronic ions Calcium and Potassium.

Though no completely satisfactory model has yet been developed for the f.c.c.-structures, this comparison provides strong support for the idea that the alcaline-earth-oxides could be treated by the same model as the alcaline-halides. The comparison proves that the experimental results can be a strong test for the calculation on models of lattice dynamics.

Furthermore, precise experimental data for the thermodynamic functions are a need, but will not change the essential features of his analysis.

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