Thermal Properties of Alkaline Earth Oxides

II. Analysis of Experimental Results for MgO, CaO, SrO, and BaO *, **

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The heat capacities of MgO, CaO, SrO and BaO, reported in part I have been analysed in terms of the frequency spectrum of the lattice with the assumption that the effect of anharmonicity of the lattice may be neglected for $T \leqq (\Theta_D/3)$.

Following the usual procedure the n-th moments of the frequency spectrum with $n = -3$, -2, -1, 0, 1 to 6 were calculated from the experimental data. From the low frequency expansion the apparent Debye characteristic temperature at 0 °K, Θ_0, is calculated to be in good agreement with Θ_0 (elast.), calculated from elasticity data. Also the limiting values at high temperatures, Θ_∞, and the zero point energy, E_z, have been calculated.

A comparison between the heat capacity data, the elastic constants and thermal properties of these oxides and the alkali-halides suggest that the interatomic forces of the alkaline-earth-oxides are rather similar to those of the alkaline fluorides. But no specific divalent character has been detected for these oxides. An appreciable anharmonic effect is present for all oxides.

1. Introduction

A number of recent attempts to understand the detailed nature of the vibrations within simple ionic solids has been successful [1]. Most of these investigations deal with the reasonably well known properties of the alkaline-halides, which have a monoionic lattice. It seemed worthwhile to extend these investigations to divalent lattices. The alkaline-earth-oxides also have a very simple structure (cubic-face-centered) which suggest relatively simple interatomic potentials. Consequently their thermal data are particularly suitable for direct comparison with the predictions of the lattice theories.

A first part of this article [2] deals with the experimental method and corresponding results for the specific heat of the alkaline-earth-oxides; in this part the results are analysed.

Although detailed informations about the frequency spectra generally cannot be obtained from inversion of the heat capacity curves, a precise knowledge of the specific heat is extremely valuable when comparing the consequences of assumptions made in various lattice theories with experimental results. BARRON [3] and his coworkers have shown the importance of the moments of the frequency distributions for the temperature variations of various thermodynamic properties; they also showed how these moments may be calculated from experimental data. We apply this method although its accuracy is limited. But at present no frequency spectra for theoretical models for the alkaline-earth-oxides nor any details about their interatomic forces are known.

Attempts to understand the nature of the anharmonic effects, present in oxides studied, have been made by different investigators [4]. A detailed analysis of these anharmonic effects together with heat capacity data above 300 °K will be discussed later.

2. Correction of Thermal Expansion

The experimental heat capacities were measured at constant pressure, c_p, The heat capacity at constant volume, c_v, may be computed from:

$$c_p - c_v = \frac{c_p}{1 + (\chi\, c_p/V\, \beta^2\, T)} \qquad (1\,\text{a})$$

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[β, volume coefficient of thermal expansion; V, molar volume; χ, compressibility].

Unfortunately, β and χ are not yet known exactly for CaO, SrO and BaO, so that some approximations are necessary. If better values become available, it will be possible to recalculate, c_v, from the primary experimental measurements and to improve the accurracy of the succeeding analysis. Nevertheless the inaccurracy does not exceed 1%.

Therefore $c_p - c_v$ have been calculated approximately from:

$$c_p - c_v = 0.0214\, c_p^2\, T/T_\mathrm{F} \tag{1 b}$$

[T_F, melting temperature; $T_\mathrm{F}(\mathrm{CaO}) = 2575\ {}^\circ\mathrm{K}$; $T_\mathrm{F}(\mathrm{SrO}) = 2415\ {}^\circ\mathrm{K}$; $T_\mathrm{F}(\mathrm{BaO}) = 2200\ {}^\circ\mathrm{K}$ [5]].

The values of $c_v(V_T)$ calculated from relation (1 a) or (1 b) correspond to the heat capacities with the volume at $T\ {}^\circ\mathrm{K}$ retained constant. In order to reduce $c_v(V_T)$ to the volume of the crystal at $0\ {}^\circ\mathrm{K}$, $c_v(V_0)$ we use the following formula [6]:

$$\Theta_\mathrm{D}(V_0)/\Theta_\mathrm{D}(V_T) = (\varrho_0/\varrho_T)^\gamma = (V_T/V_0)^\gamma \tag{2}$$

[ϱ_0 and ϱ_T, densities at $0\ {}^\circ\mathrm{K}$ and $T\ {}^\circ\mathrm{K}$; γ, Grüneisen parameter].

However, the lack of accurate values for γ (this means β and χ) of these oxides, except MgO, does not allow to introduce accurately this correction. But for MgO at 300 °K the ratio $\Theta_\mathrm{D}(V_0)/\Theta_\mathrm{D}(V_T)$ is as small as 1.005 (less than 0.5%) and even smaller at lower temperatures. A rough estimation of this ratio for CaO, SrO and BaO based on well known ϱ-data [7] gives corrections less than 0.5%.

But thermal expansion is not the only anharmonic effect that needs to be corrected. Even if the crystal is maintained at constant volume anharmonicity due to the vibrations themselves leads to contributions to the heat capacity [8] which becomes increasingly serious with increasing amplitudes of the vibrations, so that Θ_D tends to fall off for $T \geqq \Theta_\mathrm{D}/3$. This was observed for some alkali-halides [3] and has been associated with anharmonic effects, which are also present in our measurements. In order to obtain the harmonic contributions of the heat capacity for analysis of the spectrum, we therefore shall extrapolate our results below $T \leqq \Theta_\mathrm{D}/3$ to infinity (see § 3.2).

With respect to these facts the correction given by the relation (2) becomes less important and was therefore neglected. But this does not change the essential results of this analysis.

3. Analysis of the Experimental Results

In order to compare the thermal properties of the oxides, the n-th moments of the lattice vibration spectra were calculated. These moments are defined as:

$$\mu_n = \frac{1}{6N} \int_0^\infty w^n\, G(w)\, \mathrm{d}w \tag{3}$$

N, Avogadro number; w, normal mode frequency; $G(w)$, frequency distribution of the spectrum.

The mutual consistency of these moments is conveniently displayed by means of the function $w_\mathrm{D}(n)$ defined by:

$$w_\mathrm{D}(n) = \{\tfrac{1}{3}(n+3)\ \mu_n\}^{1/n};\ (n \neq 0;\ n \geqq -3). \tag{4}$$

$w_\mathrm{D}(n)$ is the maximum frequency of the Debye-distribution with the same n-th moment as the actual crystal, and which would be a constant for a Debye spectrum.

On the other hand the limiting values of $w_\mathrm{D}(n)$ as $n \to 0$ or -3 are represented by

$$w_\mathrm{D}(0) = e^{1/3}\, w_\mathrm{g} = (K\, \Theta_\infty^{(\mathrm{s})}/h) \tag{5}$$

and

$$\begin{gathered} w_\mathrm{D}(-3) = (K\, \Theta_0/h), \\ E_z = 6\, N\, h\, \mu_1/2 \end{gathered} \tag{6}$$

where w_g is the geometric mean frequency of the spectrum calculated from a high temperature expansion involving the entropy [9]; $\Theta_\infty^{(\mathrm{s})}$ gives the limiting value of the entropy at high temperatures and E_z the zero point energy of the crystal [3].

3.1. *The Low Temperature Region*

The low temperature heat capacity of an insulator can be expanded in the form:

$$C_V = a\, T^3 + b\, T^5 + c\, T^7 + \dots\ (\text{for } C_V \leqq \Theta/20) \tag{7}$$

where the coefficients a, b and c are directly related to the expansion for the frequency spectrum at low temperatures:

$$G(\omega) = 2\, N(\alpha\, \omega^2 + \beta\, \omega^4 + \partial \omega^6 + \dots) \tag{8}$$

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[5] P. Pascal, Nouveau Traité de Chimie, Vol. IV, Masson et Cie, Paris 1958.

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with

$$\alpha = \frac{15}{8}\left(\frac{a}{R\,\pi^4}\right)\left(\frac{h}{K}\right)^3; \qquad \beta = \frac{21}{32}\left(\frac{b}{R\,\pi^6}\right)\left(\frac{h}{K}\right)^6;$$

$$\gamma = \frac{15}{128}\left(\frac{c}{R\,\pi^8}\right)\left(\frac{h}{K}\right)^9;$$

(h, Planck constant; K, Boltzmann constant; R, gas constant).

The coefficient a is primarily directly related to the Debye characteristic temperature at 0 °K, Θ_0, by $a = [(2 \times 12\,\pi^4 R)/5]/\Theta_0^3$ $[J\ \mathrm{Mol}^{-1}\ (°\mathrm{K})^{-4}]$ and secondly to $w_\mathrm{D}(-3)$ by Eq. (6). Θ_0 is readily derived from a, determined best by a graph (C/T) vs. (T^2). The coefficients b and c were determined by least square fitting of the experimental data to Eq. (7) or by plotting (C/T^3) vs. (T^2).

The corresponding coefficients and Θ_0, derived from the present analysis are given in Table 1 and presented in Fig. 1.

Parameter	MgO	CaO	SrO	BaO
θ_0	945 ± 1	605 ± 2	401 ± 0.5	232 ± 0.5
θ_0 (elast.)	949	620	—	—
a	0.4618	1.7412	6.002	28.92
$b \cdot 10^6$	0.227	6.239	42.06	821.2
$c \cdot 10^9$	0.1729	28.47	773.4	9206
$\alpha \cdot 10^{39}$	1.186	4.469	15.45	74.50
$\beta \cdot 10^{65}$	0.5830	13.17	88.40	723.0
$\gamma \cdot 10^{91}$	1.512	249.0	6450	81030

Table 1. The coefficients of the low temperature heat capacity and of the low temperature frequency spectrum and the comparison of Θ_0 and Θ_0 (elast.).

The Θ_0-values for MgO and CaO derived from the elastic constants have been calculated by different methods, indicated also in Table 1.

The agreement between Θ_0 (cal) and Θ_0 (elast) is only very good for MgO. For CaO there is a difference of about 3%, however it should be remembered that Θ_0 (elast) for CaO has been calculated from the elastic constants at room temperature. For SrO and BaO no experimental data for the elastic constants are yet available.

3.2. The High Temperature Region

The high temperature expansion for the equivalent Debye characteristic temperature, derived from the expansion of the heat capacity as a power series [10] in $1/T^2$ can be used to determine the first few even moments of the spectrum. This series in $1/T^2$ which converges rapidly at low temperatures may be written in the form [11]:

$$\Theta_\mathrm{D}(V_0)^2 = \Theta_\infty^2\left\{1 - A\left(\frac{\Theta_\infty}{T}\right)^2 + B\left(\frac{\Theta_\infty}{T}\right)^4 - + \ldots\right\}$$

where (9)

$$\Theta_\infty = \left(\frac{h}{K}\right)\left(\frac{5\,\mu_2}{3}\right)^{1/2}, \tag{10}$$

$$A = \left(\frac{3}{100}\right)\left(\frac{\mu_4}{\mu_2}\right) - \frac{25}{21}\Bigg); \; B = \frac{1}{1400}\cdot\left\{\left(\frac{\mu_6}{\mu_2} - \frac{125}{81}\right) - 100\,A\right\}$$

and μ_2, μ_4, μ_6 are even positive moments.

The value for Θ_∞ was derived from a plot $\Theta_\mathrm{D}(V_0)^2$ vs. $(1/T_2)$ by extrapolating the curve to the intercept $1/T^2 = 0$; the coefficients A and B were determined again by a least square method and by the plot of

$$\left[1 - \left(\frac{\Theta_\mathrm{D}}{\Theta_\infty}\right)^2\right] \Big/ \left(\frac{\Theta_\infty}{T}\right)^2 \text{ vs. } \left(\frac{\Theta_\infty}{T}\right)^2$$

in the range of $\Theta_\mathrm{D}/6 < T < \Theta_\mathrm{D}/3$; the intercept of the curve with the axis gives A and its slope gives $-B$.

Parameter	MgO	CaO	SrO	BaO
θ_∞	$776 + 2$	$605 + 4$	$446 + 5$	$370 + 4$
$A \cdot 10^4$	29.0	80.0	160.0	277.5
$B \cdot 10^4$	0.50	1.45	4.20	6.10
θ_∞	779	579	417	302
$w_\mathrm{g} \cdot 10^{13}$	1.164	0.8661	0.6230	0.4513
S (J/Mol) 0 °C	27.19 ± 0.1	38.3 ± 0.1	51.9 ± 0.1	66.9 ± 0.1
E_z	14700	11200	8050	6250

Table 2. The values of Θ_∞, A, B and $\Theta_\infty^{(\mathrm{s})}$, the geometric mean frequency w_g, the entropie, S, and the zero point energy, E_z.

Reduced frequency $w(n)$	MgO	CaO	SrO	BaO
$w(-3)$	1.968	1.261	0.837	0.485
$w(-2)$	1.760	1.215	0.815	0.510
$w(-1)$	1.670	1.200	0.820	0.565
$w(0)$	1.623	1.210	0.851	0.630
$w(1)$	1.623	1.230	0.871	0.691
$w(2)$	1.620	1.265	0.921	0.772
$w(4)$	1.635	1.340	1.050	0.891
$w(6)$	1.680	1.378	1.069	0.945

Table 3. The reduced frequency spectrum of the alkaline earth oxides (frequencies of the Debye distribution with the same n-th moments).

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[10] H. THIRRING, Phys. Z. **14**, 867 [1913].

[11] C. DOMB and L. SALTER, Phil. Mag. **43**, 1083 [1952].

3.3. The Intermediate Temperature Region

In addition to the moments μ_2, μ_4, μ_6 obtained from Eq. (9) other moments of the frequency spectrum can be calculated from integrals of the form [12]:

$$\frac{1}{6NK}\int\frac{c_v(V_0)}{T^n}\,\mathrm{d}T=\Gamma(n+1)\,\xi(n)\,\mu^*_{1-n}-\frac{1}{n-1}\cdot\frac{1}{T^{n-1}}+\sum_{s=1}^{\infty}(-1)^{s+1}\frac{B_{2s}}{(2s)!}\cdot\frac{2s-1}{2s+n-1}\cdot\frac{\mu^*_{2s}}{T^{2s+n-1}} \tag{11}$$

where $\Gamma(n+1)$ is the gamma function, $\xi(n)$ the Rieman zeta function, B_{2s} the Bernoulli numbers and $1<n<4$. The numerical values deduced from the above analysis are given in Table 2 and 3.

4. Discussion of the Results of the Present Analysis

A direct comparison of the experimental frequency spectrum and a theoretically calculated one would be the best analysis. However no frequency spectra for theoretical modes corresponding to these oxides are at present available for comparison and very little appears to be known in detail about the interatomic forces. But by comparing the present results with those obtained for monovalent ionic crystals and with some general relations between Debye temperature and crystalline parameters we may see any significant differences.

4.1. Θ_0 and Θ_∞ as Function of Mass and Lattice Parameters

The limiting value Θ_0 is given by a complicated function of the elastic constants, A, involving the interatomic forces, the density and the value of a unit cell [3, 13]:

$$\Theta_0\sim\left[\frac{A'}{\varrho^{3/2}\,V_c}\right]^{1/3}=\frac{A}{a\sqrt{M}} \tag{12}$$

[M, molecular mass; a, lattice distance in the cubic structure].

Assuming that the interatomic forces are identical for all oxides, A should be constant and Θ_0 a function of $(a\sqrt{M})^{-1}$ only. This is shown in Fig. 1 where Θ_0 as function of $a\sqrt{M}$ is plotted.

An equal relation exists at high temperatures [14]:

$$\Theta_\infty\sim 1/\sqrt{M^*}\,. \tag{13}$$

Eq. (13) holds, if all ions are submitted to the same effective field in the crystal; M^* is the reduced mass of the molecule: $(M^{-1})^*=(m^{-1})_{\mathrm{An.}}+(m^{-1})_{\mathrm{Kat.}}$.

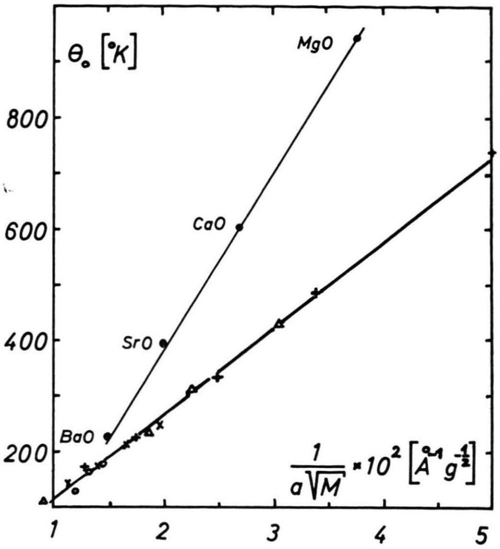

Fig. 1. Debye temperature Θ_0 at 0 °K of the alkaline earth oxides and alkaline halides as function of $a\sqrt{M}$ (a, lattice parameter in the cubic structure; M, molecular mass). + alkaline fluorides, △ alkaline chlorides, × alkaline bromides, ○ alkaline iodides.

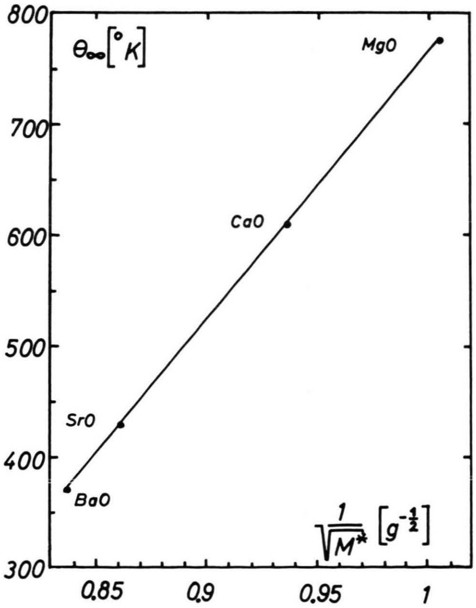

Fig. 2. Debye temperature Θ_∞ at high temperature of the alkaline earth oxides as function of the reduced molecular mass, M^*.

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[12] J. L. Hwang, J. Chem. Phys. **22**, 154 [1954], and Ref. [3].

[13] Eq. derived in Ref. [3].

[13] M. Blackmann, Handbuch der Physik, Vol. **7** (1) [1955].

[14] M. Blackmann, Proc. Roy. Soc. London **181**, 58 [1942].

Figure 2 shows that Eq. (13) is correct also for the alkaline-earth-oxides.

From Figs. 2 and 1 we conclude that the interatomic forces in these oxides are quite identical, even more, the same relations (13) and (12) are correct also for the alkaline-halides (e. g. see Fig. 1). In conclusion we can say that the interatomic forces between alkaline-earth-oxides and -halides are rather similar.

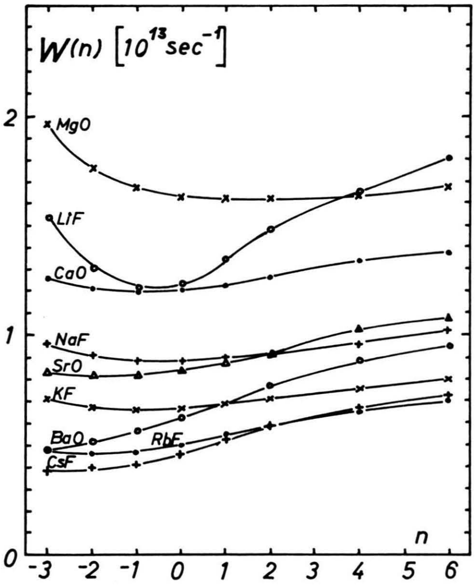

Fig. 3. Reduced frequency spectrum $w(n)$ as function of n for the alkaline earth oxides and the alkaline fluorides.

4.2. *Reduced Frequency Spectrum $w_D(n)$ versus n*

It is not adequate to discuss the frequency spectrum itself in terms of the function $w_D(n)$, because this function is relatively insensitive to the shape of the spectrum.

It is easily seen from Fig. 3 that the effect of the masses of the constituent ions may be remarkably reflected in the function $w_D(n)$ rather than in the frequency spectrum itself. The absolute value of $w_D(n)$ increases with decreasing mass of the anion in a series of compounds having the same cation. Comparatively appreciable differences between the shape of $w_D(n)$ in Fig. 3 leads to the following conclusions.

Both the steady increase in the ratio of higher to lower moments and the decreasing curvature of the $w_D(n)$ curve between $n=-3$ and $n=0$ on going from MgO to BaO presumably indicate a gradual increase in the density of modes at higher frequencies in the spectrum.

However the increasing values of the coefficients a, b and c indicate that the deviation of the $w_D(n)$-spectrum from a pure Debye spectrum $[G(\omega) \sim \omega^2]$ increases on going from MgO to BaO. This means that the number of modes of the vibrations spectrum $w_D(n)$ rises quicker at low frequencies for BaO than for MgO but the mean part of the spectrum extends to higher reduced frequencies.

This behaviour is equal to that of the alkaline-halides [15] having the same cation. Their spectra and their equivalent moments have been calculated by KARO [15] and partially proved experimentally.

Comparing the present moments of the oxides with those of the alkaline-halides this shows that the ratio of the moments:

$$\frac{w_D(n_i;\,\mathrm{BaO})}{w_D(n_i;\,\mathrm{CsF})}\,;\ \frac{w_D(n_i;\,\mathrm{SrO})}{w_D(n_i;\,\mathrm{RbF})}\,;$$

etc. are nearly constant.

This means that the interatomic forces in both series of oxides and fluorides are virtually identical and we conclude that the oxides may be treated theoretically with the same models as the well established properties of the alkaline halides.

The series of curves $w_D(n)$ versus n in Fig. 3 reveal that the variation for positive values of n is lee marked and the curve flattened over considerably wide ranges if the mass ratio of the constituent ions approaches unity; i. e. MgO for the oxides, NaF for the fluorides. This observation suggests that the actual spectrum approximates more closely to the Debye-distribution as the masses of the components becomes close to unity.

It should be noted that $w_D(n)$ rises more rapidly as $n \rightarrow -3$ for MgO than for BaO; the minimum of the curve shifts to higher n-values in the same direction. It is not yet clear if this effects are due also to the ratio of masses.

4.3. *Variation of the Reduced Debye Temperature with Reduced Absolute Temperature; Effect of Mass Factor*

A further correspondence between oxides and fluorides at both high and low temperatures is offered by examining the reduced Debye temperature $(1-\Theta_D/\Theta_0)$ as a function of T/Θ_0, given in Fig. 4.

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[15] A. M. KARO, J. Chem. Phys. **33**, 7 [1960].

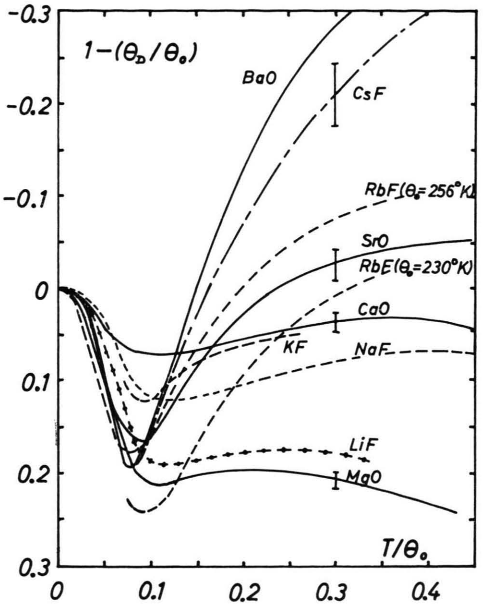

Fig. 4. Deviation of the reduced Debye temperature $[1-(\Theta_D/\Theta_0)]$ from the value at 0 °K as function of reduced temperature, T/Θ_0, for the alkaline earth oxides and alkaline fluorides. *I* indicates the influence of an error of 10 °K in Θ_0.

The mass factors of oxides and fluorides are very close together. With the assumption of identical interionic forces, this implies nearly identical variations of $(1-\Theta_D/\Theta_0)$ with T/Θ_0 for large $T (T/\Theta_0 > 1/5)$. The coefficient A [Eq. (10)] is the most clearly defined parameter at high temperatures in describing the departure of Θ_D from Θ_∞ A should be very sensitive to the type of interatomic forces [3, 13], but less sensitive to the mass ratio. However experimentally it was found to vary smoothly with the mass ratio for the alkaline halides. The same relation fits surprisingly well to the considered oxides; this is shown in Fig. 5.

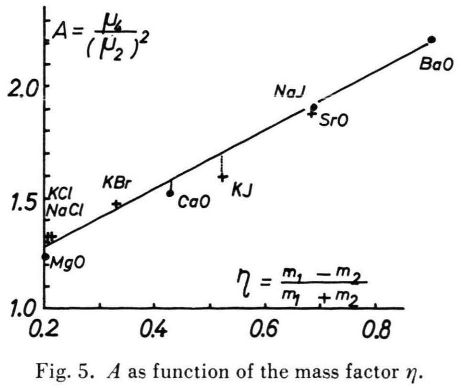

Fig. 5. A as function of the mass factor η.

At low temperatures the effect of the mass ratio is less important and the shape of the curve of $(1-\Theta_D/\Theta_0)$ is mainly influenced by the elastic constants; nevertheless the behaviour of the oxides is again remarkably similar to that of the alkaline fluorides. With increasing mass ratio the departure of Θ from Θ_0 for both types of compound becomes slower if $\Theta_\infty/\Theta_0 < 1$ (i. e. MgO → CaO; LiF → NaF); but then more and more quickly for Θ_∞/Θ_0 → CsF). Indeed, the ratio of elastic constants > 1 (i. e. CaO → SrO → BaO; NaF → KF → RbF) C_{11}/C_{44} and C_{12}/C_{44} is quite close for LiF and MgO, NaF and CaO; this is shown in Table 4 (C_{ii}-data from Ref. [16]).

	C_{11}/C_{44}	C_{12}/C_{44}
LiF	1.920	0.653
MgO	1.906	0.541
NaF	2.9	0.9
CaO	2.9	0.9

Table 4. Comparison of the elastic constants of LiF, MgO, NaF and CaO at low temperatures.

Note also that the initial decrease in Θ_D with temperature (from Θ_0 to higher temperatures and from Θ_∞ to lower temperatures) leads to a minimum near $(T/\Theta_0) \approx 0.1$, which is strongly mass dependent:

$$T/\Theta = 0.11 \text{ for MgO; } 0.105 \text{ for CaO;}$$
$$0.09 \text{ for SrO; } 0.075 \text{ for BaO;}$$

No theoretical explanation for this phenomena is yet known.

Unfortunately existing heat capacity data for the fluorides are not available or are not quite accurate enough to allow a more detailed comparison. Also the lack of reliable elastic constant data for the oxides prevents actually more precious conclusions to be drawn. Nevertheless it seems that there is no question that these oxides show the same type of interionic forces as the alkaline fluorides and that the same theoretical models as well established for these compounds could be applicated.

Finally note that the gradual decrease in Θ_D observed in all oxides (as also in most part of the alkaline-halides) at higher temperatures may be attributed to an increase in the heat capacity due to positive anharmonic effects of the vibrations themselves.

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[16] J. T. Lewis, A. Lehoczky, and C. V. Briscoe, Phys. Rev. **161**, 877 [1967].

5. Conclusions

A set of experimental heat capacities for the alkaline-earth-oxides, reported in part I was analysed. From the results it was shown:

- that there is a systematic change in the shape of the vibration frequency spectra, which is virtually identical to those of the alkaline fluorides, having nearly the same mass ratio as the oxides and having the same ratio of elastic constants at low temperatures;
- that therefore the oxides do not exhibit any specified divalent ionic character;
- that all oxides show a positive anharmonic contribution to the specific heat, which was excluded in this analysis.

If this qualitative interpretation of the results seems clear a quantitative discussion of these results is not yet possible, due to the lack of accurate experimental data on density, elastic constants, coefficient of dilatation and compressibility and their variation with temperatures for these oxides as for the fluorides; and finally there is a need for the exact frequency spectra, which should be deduced from neutron scattering data. In connection with these experimental data more detailed studies of the lattice dynamics of alkaline-earth-oxides should be required.

Thermoelectric Properties in Silver Chloride–Alkali Chloride Fused Mixtures *

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The initial thermoelectric power of the molten salt mixtures (Ag+Me) Cl (Me=Li, Na, Rb, Cs) has been measured at various temperatures around 800 °C using a silver electrode thermocell. In addition the thermoelectric power of molten pure AgCl is reported.

These data have been used to obtain relative values of the heats of transport of the alkali cations in pure salts. Moreover the global behaviour of these mixtures in respect to an ideal model for the heat and electricity transport is discussed.

Though the first measurements of thermoelectric power in molten salts date back to the end of the last century, systematic work has appeared only recently. HAASE [1] has given a concise discussion of the data presented in the literature. For a full phenomenological description of the system, initial and stationary state values of the thermoelectric power would be desirable. Nevertheless, as it has already been shown [2], values of thermoelectric power at zero time in molten binary mixtures enable to draw some information on the global behaviour of the systems in respect to the heat and electricity transport phenomena.

This work reports measurements of the thermoelectric power at zero time on the molten binary mixtures $AgCl + MeCl$ where $Me = Li$, Na, Rb, Cs. The system $AgCl + KCl$ has previously been described [3].

The surveys have been made in the thermocell:

$$\text{final stage} \mid Ag_{(s)} \mid (Ag + Me)\,Cl_{(l)} \mid Ag_{(s)} \mid \text{final stage} \qquad (1)$$

at various temperatures around 800 °C and at different compositions.

Experimental

The "U" shaped cell, made of quartz, was placed in a nickel block divisible into three pieces. The differential heating of one of the two arms of the cell was obtained by means of thermocoax resistences (Sodern). An electrode-holder was placed in each of the two arms of the cell to support the point shaped silver electrode. The measuring thermocouple in platinel was placed near the electrode and shielded by a thin quartz tube. The differences in temperature ranged from 5 to 15 °C. All the other experimental features were analogous to those described in previous works [2, 3].

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