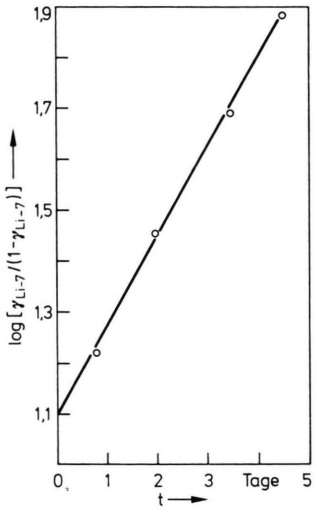

Abb. 3. Zeitlicher Verlauf der Li-7-Anreicherung.

lagert, die durch den Einfluß der Komplexbildungsgleichgewichte in homogener Phase entstehen.

Als Beispiel zeigt die Abb. 3 eine Li-7-Anreicherung im Bereich hoher Konzentration. Die stationäre Konzentration des verwendeten Lithiumacetatsalzes stellte sich den gewählten Betriebsdaten entsprechend auf 0,45 N ein. Das Verhältnis Zulaufrate $\dot{M}$ /Kammervolumen V betrug $2\,h^{-1}$. Nach 4,5 Tagen reicherte sich Li-7 in der Kammer K_2 der abgebildeten Trennsäule auf 98,7% an. Bis zu diesem Zeitpunkt verlief die Anreicherung noch im linearen Bereich. Aus der Neigung der Geraden ergibt sich für den Elementareffekt $\Delta u/\bar{u}$ der Li-Isotope nach der Gleichung

$$\Delta \log \frac{\gamma_{\text{Li-7}}}{1-\gamma_{\text{Li-7}}} \approx 0{,}434 \cdot \frac{\dot{M}}{V} \cdot \frac{\Delta u}{\bar{u}} \Delta t$$

der Wert $2 \cdot 10^{-2}$, während er in 0,05 n. Lösung $2{,}9 \cdot 10^{-3}$ beträgt (vgl. [4], S. 72).

Thermal Properties of Alcaline-Earth-Oxides

I. Specific heat measurements [1–3]

E. GMELIN [4]

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(Z. Naturforsch. **24 a**, 1794—1800 [1969]; received 20 June 1969)

The heat capacities of MgO, CaO, SrO, BaO, having NaCl-structure, have been measured with an adiabatic calorimeter capable to measure heat capacities of solids between 1.2 and 340 °K. A mechanical thermal switch is used for specimen cooling and the temperature calibration above 4 °K is performed with a gas thermometer.

The values of the specific heats, C_p, are tabulated. The entropies at 273.15 °K are 27.19; 38.3; 51.9; and 66.9 for MgO, CaO, SrO and BaO respectively, in J/mol °K. The accuracy of the measurements is estimated to be better than 0.8% (smoothed curve).

The alkaline earth oxide crystals have a very simple structure which suggests relatively simple interatomic potentials. Consequently their experimental thermal data are particularly suitable for the direct verification of the lattice dynamic theories. They form a class of oxides which have a common cubic face centered NaCl structure, except BeO which has a hexagonal compact structure and was discussed recently [5]. Because these solids have basically the same ionic binding, a relatively smooth primarly mass dependent relationship should exist between their thermodynamic properties. Similar correlations have been observed in the well established low temperature thermal properties of the alkaline halides (for further references see ref. [6]). Unfortunately the low temperature specific heat of the alkaline-earth-oxides (except those of MgO) are not well known below 70 °K. The existing data

[1] Part I and part II of this work is dedicated to Professor H. GOBRECHT to his 60th birthday.

[2] These results have been communicated partially at the „Frühjahrstagung des Regionalverbandes Bayern der Deutschen Physikalischen Gesellschaft", 17—21 March 1969.

[3] This work has been done in a partial-fulfillment of a "Thèse d'Etat ès Science" at the university of Grenoble.

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[5] E. GMELIN, C. R. Acad. Sci. Paris **262**, 1452 [1966].

[6] A. J. KIRKHAM and B. YEATES, J. Phys. C **1**, 1162 [1968]. — M. SOVAI, J. Phys. Soc. Japan **25**, 421 [1968].

Material	Authors	Ref.	Measured Temperature range (°K)	Remarks	Error (%)	Sample impurities in ppm
MgO	BARRON, BERG, MORRISON	7	20—300		1	< 1000
	GMELIN	8	1— 36		< 0.8	< 850
	GUNTHER	9	80—300	only several points	—	—
	PARKS, KELLEY	10	80—300		1	< 5000
	ARCHIBALD, GIAUQUE	11	20—300	effect of particle size visible	—	—
CaO	NERNST, SCHWERS	12	77—300	differences	—	—
	PARKS, KELLEY	10	40— 80	up to 10%	1—2	12000
	GMELIN	5	1— 80		< 0.8	< 1500
SrO	ANDERSON	13	77—300		1—2	—
BaO	ANDERSON	13	77—300		1—2	—

Table 1.

which show a rather large scatter are listed in Table 1 and will be compared with the present results later.

The specific heat of MgO shows a rapid decrease of the equivalent Debye temperature, Θ, at low temperatures (<100 °K) with increasing temperature. A small minimum value of Θ is reached near $T/\Theta \sim 1/10$ (100 °K). At higher temperatures Θ is nearly constant. However the Θ values for CaO are nearly constant between 70 °K and 280 °K, while the Debye temperatures of SrO and BaO decrease more and more rapidly down from room temperatures; at 77 °K no minimum value for Θ is yet visible.

The purpose of this work is to explain the somewhat discordent results and to obtain precise data for the specific heat of the alkaline earth oxides in the temperature range from 1.2 °K to 340 °K for comparison with existing data and in particular for analysing precisely the specific heats in terms of the frequency spectrum of the crystal lattice.

I. Experimental

Calorimeter

The essential features of the adiabatic calorimeter and the cryostat, permitting to measure hat capacities between 1.2 and 340 °K has been described in detail in a recent publication from this laboratory [8]. Briefly the measuring technique is an isothermal method, using a double walled calorimeter, wherein the inner calorimeter is regulated with a semiautomatic temperature control circuit up to better than 1% of the specimen temperature during a heat capacity measurement. In order to prevent the adsorption of Helium on the powder-sintered samples a mechanical-thermal contact cooling method [8] instead of the heat exchange gas has been used.

Only some special features for measuring the oxides should be indicated:

The thermometer and heater resistances are mounted on the specimen holder. An Allen-Bradley, 1/10 W, 47 Ω, carbon resistor is used as working thermometer between 1 and 20 °K; at higher temperatures measurements are performed with a platinum resistor (Rosemount Eng. Comp.). The currents across these resistances have been selected as to render maximum accuracy; 1 to 10 μA in the liquid Helium-region, 20 μA near 20 °K for the carbon resistance and 1 to 5 mA for the platinum resistance in the whole temperature range.

The heater is formed of a 1000 Ω strain free constantan wire, wound directly, non-inductively on the holder and anchored there with Araldite. The heating current varies continuously between several μA and 300 mA. An asymmetrical method of connecting the heater leads to the heater was adopted to eliminate errors due to the heat generated in the leads [8].

To avoid an "overshoot" of the temperature after a heat pulse two separated specimen holders (clamping rings) have been used, one having incorporated the thermometers only, the other one, on the other end of the specimen, the heater only. Good thermal contact between specimen and holder is ensured with a little amount of Apiezon-N-grease. Samples are weighed to ± 1 mg initially and again after removal from the calorimeter, also the sample holder. Any increase in weight is presumed to be due to the grease which adheres to the sample.

[7] T. H. K. BARRON, W. T. BERG, and J. A. MORRISON, Proc. Roy. Soc. London A **250**, 70 [1959].
[8] E. GMELIN, Cryogenics **7**, 225 [1967].
[9] P. GUNTHER, Ann. Phys. **51**, 838 [1916].
[10] G. S. PARKS and K. K. KELLY, J. Phys. Chem. **30**, 47 [1926].
[11] W. R. GIAUQUE and R. C. ARCHIBALD, J. Am. Chem. Soc. **59**, 561 [1937].
[12] W. NERNST and F. SCHWERS, S.B. Deutsch. Akad. Wiss. Berlin 355 [1914].
[13] A. ANDERSON, J. Am. Chem. Soc. **57**, 429 [1935].

Determinations of the heat input and the thermometer resistance were made with a double potentiometer, measuring voltages and currents across the resistances, each with an accuracy of 0.02%.

Before and after the heating period the drift of the specimen temperature is observed for about 5 to 10 times of the heating time, varying between 10 s to 5 min. The temperature drifts usually vary between 0 and $5 \cdot 10^{-5}$ °K/s so that the changes of temperature during the drift-periods are less than 5% of the temperature increment.

The long term linear drift rates are used in the conventional manner to determine the change of temperature ΔT of the sample at the midpoint of the heat pulse. In general the temperature increments were chosen to be of the order of 0.05 T to make errors due to the temperature variation of the heat capacity smaller than those involved in the determination of ΔT (0.1%).

The attainment of a constant tempertaure became increasingly slower above 150 °K presumably due to the poor thermal conductivity of the powder-sintered samples at higher temperatures. So sometimes one measured point needed 3/4 to 1 h.

Measurements between 10 °K and 80 °K were made partially by a continuous warming method, using the same calorimeter assembly with an automatic temperature control device for the thermal shield (inner calorimeter). So no temperature difference between specimen and calorimeter existed and the temperature drift of the sample was zero. Than the speed of temperature rise at constant heat input is directly related to the specific heat. Using this system data can be obtained very rapidly. The accuracy of these experiments was at least as high as had been attained with the usual heat burst method. But above 80 °K due to the poor thermal conductivity of the samples, this method introduces systematical errors.

Thermometry

The carbon resistance thermometer has been calibrated for each experiment by admitting exchange gas into the calorimeter and taking a set of 20 to 25 calibration points in the range 1.2 to 4.2 °K and 4.2 to 20 °K.

Calibration was performed in the liquid helium range against the vapor pressure of helium (NBS-Temperature scale of 1958). In the temperature range between 4.2 and 20 °K the resistance was calibrated against a constant volume gas thermometer with the fix point at 4.2 °K as described in detail elsewhere [8]. The agreement between the temperature indicated by the platinum resistance and that of the gas thermometer is within 5 m °K near 20 °K and within 40 m °K at 80 °K.

To calculate T an adequate functional relationship between resistance, R, and temperature, T, should be known. The calibration data between 1 and 4 °K were fitted to a five parameter equation:

$$1/T_c = \sum_{n=-3}^{1} a_n \log R^n$$

and the coefficients a_n calculated by a least square method. For the calibration points above 4 °K an interpolation formula $1/T_a = a + b \ln R$ was used for a first approximation. Then a polynomial:

$$T_c = T_a + \sum_i C_i T^i \quad (i = 1, \ldots, 5)$$

was applied to fit the calibration curve. The coefficients a, b, and c_i were also calculated by a least square method. The difference between the calculated temperatures, T_c, and the experimental values, T, is less than 2 m°K near 4 °K and at worst 10 m°K near 20 °K.

The curve $(T - T_c)$ vs. T is a very precise check of the reliability of the calibration and shows directly the systematic error, caused by the temperature calculation. If there are any systematic deviations in this curve instead of a random scatter of the calibration points around the calculated temperature curve the slope of the curve $\Delta(T - T_c)/\Delta T$ is equal to the error introduced in the specific heat. This error was always made to be less than 0.2%.

Addenda Heat Capacity

The addenda heat capacity is determined always separately in the whole temperature range with the same accuracy as for the sample heat capacity. Therefore the two clamping rings of the specimen holder are screwed together. Separate addenda runs were made which were separated by measurements on various samples (irradiated BeO-specimens [14] and alkaline earth oxides containing iron impurities [15]). The random scatter of the different runs is less than 1% and no systematic deviations between the different experiments could be detected. The data for all addenda runs were treated as equivalent and were least square fitted to a power series below 30 °K.

The incertainty due to the addenda corrections [16] (Apiezon N grease) is less than 0.2%. However the incertainty in the total addenda heat capacity (the same as for the specimen with holder measurement which is discussed in the next paragraph) could introduce significant incertainties into the low temperature heat capacity of the specific heat of the specimen. The heat capacity of the specimen holder only was at most 70% of the total near 2 °K, and 45% near 5 °K, in the most unfavourable case of MgO, and gradually decreased to 30% of the total near 80 °K.

Experimental Accuracy

The different experimental incertainties of the specific heat measurements are listed in Table 2.

The random error in the individual heat capacity measurement is essentially due to the extrapolation of the drift lines for the determination of ΔT of the heat

[14] E. GMELIN, Thèse d'Etat ès Sciences, Grenoble 1968, to be published.

[15] E. GMELIN, J. Phys. Chem. Solids, to be published.

[16] E. F. WESTRUM et al., Cryogenics 7, 43 [1967].

	Incertainty
Incertainties in voltage and current measurements	$< 0.1\%$
in heating time	$< 0.1\%$
Random error of an individual heat capacity measurement	$\sim 1\%$
Systematic errors	$< 0.5\%$
Incertainty in the addenda heat capacity	$< 1\%$
Total incertainty of the smoothed specific heat curve for MgO and CaO	$< 0.8\%$
for SrO and BaO	$< 0.5\%$

Table 2.

pulses. The experimental data usually scatter randomly from a smooth cuve by about the calculated random error in the whole temperature range. The scatter is utmost 4% for the smallest sample (MgO) at the lowest temperatures, $T < 2$ °K, and 1% for all higher temperatures. Systematic errors are almost entirely due to incertainties in the temperature scale. Periodic systematic checks were made to ascertain the effects of varying the heating time and range of temperature increment, but no observable effects were found.

This error estimate is based in part upon the specific heat results received with the same calorimeter from a high purity copper sample of the "1965 Calorimeter Conference Copper Standard". The accuracy and reliability of the present measuring apparatus has been checked with the "Standard sample T 4.4" [17]. Agreement between the results and those of other investigators was within the experimental error of $\pm 0.3\%$.

Sample Preparation

All samples were cylindrical shaped with various diameters and different lengths. The main characteristics and the preparation techniques of the measured specimens are shown in Table 3; these are: material, preparing, main impurities, weight.

Material	Preparation	Impurities in ppm	Sample weight in mol
MgO	powder-sintered	Total < 1000	
	2 h at 1300 °C	SiO_2 500; C_2O_3 200	1.3038
	than 2 h at 1500 °C	Na_2O 30; K_2O 20	
	than 2 h at 1850 °C	Fe, Co, Ni < 10	
CaO	powder-sintered	Total < 300	
		B ~ 30	0.7896
		Fe, Co, Ni < 10	
SrO	powder-pressed	Total < 20000	0.4013
BaO	powder-pressed	Total < 3000	
		Chlorines 500;	
		Sulfides 20;	0.3149
		Metals 50;	
		Fe, Co, Ni < 20	

Table 3.

[17] K. H. GOBRECHT u. E. GMELIN, Z. Angew. Phys. **24**, 21 [1967].

MgO, CaO

All physical and chemical characteristics and the technical preparation of these samples have been described in previous papers, dealing with their very low temperature heat capacities (MgO [8]; CaO [5]).

SrO, BaO [18]

Powders of the purity given in Table 3 were pressed with 7 to/cm² in a press of 30 mm diameter. The grain size of the powders was several hundred microns. Actually it was not possible to get these oxides with less impurities. But the metal impurities are quite small and no influence of ferromagnetic ions on the measured heat capacity has been observed; however this was the case for several hundred ppm of iron ions in MgO [15].

We did not sinter these specimens, because they volatilize very quickly at higher temperatures before sintering. However their thermal conductivity was good enough, for measuring precisely their specific heats.

The investigated materials exhibited certain experimental difficulties since they are rather hygroscopic. Therefore the CaO and SrO samples have been mounted in the calorimeter vessel by using an inert gas atmosphere.

X-ray investigations of the powders showed that all specimens are cristallized in the cubic-face-centered form.

II. Results

The results for MgO, CaO, SrO and BaO in the region 1.2 to 4.2 °K are plotted in Figures 1 to 3. In this temperature range the "Debye-T^3-law" is valid $C_p = (\alpha/\Theta^3)T^3$. From the slope of the straight lines the corresponding Debye temperature Θ_0 at 0 °K is directly deduced to be:

$$\Theta_0(\mathrm{MgO}) = 945 \pm 1\ ^\circ\mathrm{K},$$
$$\Theta_0(\mathrm{CaO}) = 605 \pm 2\ ^\circ\mathrm{K},$$
$$\Theta_0(\mathrm{SrO}) = 401 \pm 0.5\ ^\circ\mathrm{K},$$
$$\Theta_0(\mathrm{BaO}) = 232 \pm 0.5\ ^\circ\mathrm{K}.$$

Curve II and III for CaO presents results on samples which have been stored for 1 month and 3 months respectively on air and not in vacuum. The "apparent electronic" contribution to the specific heat is due to Ca $(OH)_2$ formation and water absorption in the sample, however an exact explication can not be given yet. This needs further systematic investigations.

For the temperature region above 4 °K the experimental points are shown in Figures 4 to 8, where

[18] Furnished by SERLABO, Paris, from MERCK A.G., Darmstadt, Germany.

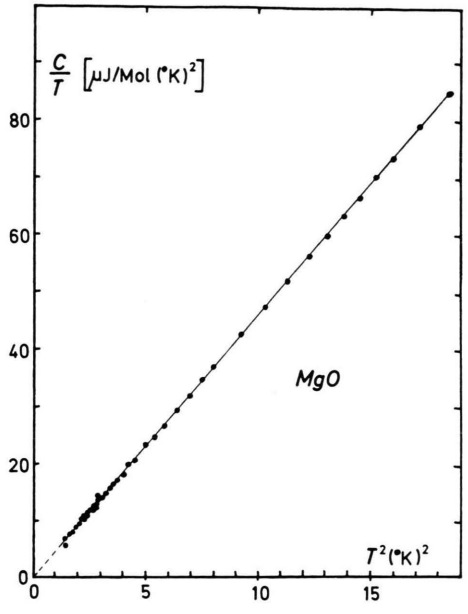

Fig. 1. Specific heat C_p vs. T of MgO as a function of T^2.

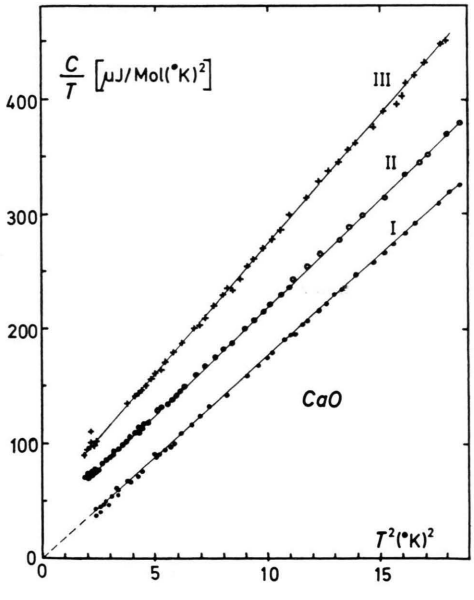

Fig. 2. Specific heat C_p vs. T of CaO as a function of T^2. I: CaO pure; II: CaO, having been on air for 1 month; III: CaO, having been on air for 3 months.

the equivalent Debye temperature Θ as a function of absolute temperature T is plotted. It is often useful to describe the heat capacity of solide in terms of the Debye theory, as in this way small differences in the type of temperature dependence of the specific heat of different substances are clearly exhibited which is not the case in a C_p vs T or $\log C_p$ vs $\log T$

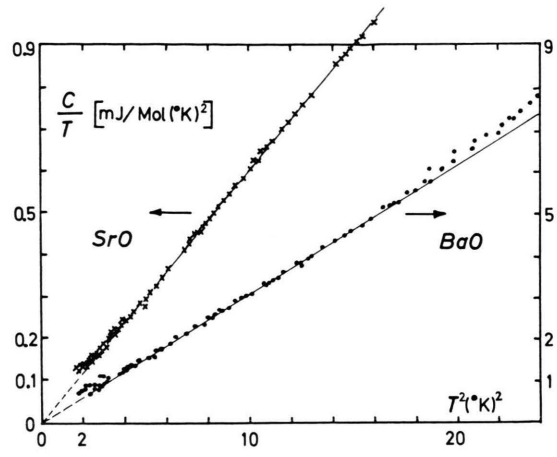

Fig. 3. Specific heat C_p vs. T of SrO and BaO as a function of T^2.

representation. These Θ values are directly calculated from the experimental C_p-data (specific heat at constant pressure); the correction to C_v, important only at higher temperature ($T > \Theta/3$) is shown as smoothed dotted line in Figures 4 to 8. Table 4 list interpolated numerical values $C = f(T)$. The molecular weights are based on the 1966 JUPAC report on atomic weights. Table 5 gives the values of the entropy of the alkaline earth oxides at 273.15 °K.

	MgO	CaO	SrO	BaO
S	27.2 ± 0.1	38.3 ± 0.1	51.9 ± 0.1	65.9 ± 0.1

Table 4. Heat capacity of MgO, CaO, SrO, BaO.

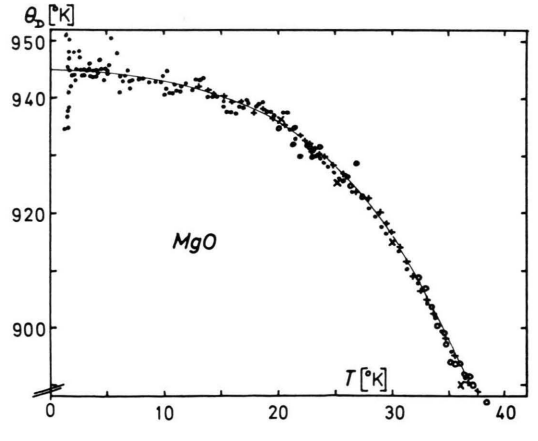

Fig. 4. Debye temperature Θ of MgO as a function of absolute temperature T in the low temperature region. ● experimental points, measured with carbon resistors; ○ experimental points, measured with platinum resistors; + experimental points, measured with the continuous warming method; × BARRON, BERG, MORRRISON [7].

T (°K)	C_p (mJ/Mol °K) for MgO	~ CaO	SrO	BaO
4	0.2936	1.121	3.592	1 936
5		2.191	7.551	41.60
6	0.9953	3.805	13.11	70.00
6	0.9952	3.805	13.11	70.00
7	1.592	5.950	22.49	122.3
8	2.415	8.8852	34.50	193.4
9	3.421	13.21	50.72	287.6
10	4.750	18.55	70.08	417.1
15	15.95	63.82	271.3	1 904
20	38.22	150.5	682.3	4 500
25	76.65	300.5	1 460	6 890
30	137.2	552.0	2 751	9 098
40	368.4	1 354	6 124	12 830
50	829.2	263	9 349	16 690
60	1 612	4 720	12 640	20 310
70	2 809	7 090	16 010	23 850
80	4 398	9 610	19 290	27 030
90	6 327	12 020	22 110	29 650
100	8 281	14 700	24 910	31 880
110	10 200	17 200	27 420	33 990
120	12 300	19 580	29 930	35 680
130	14 290	21 820	31 550	35 980
140	16 300	24 070	33 460	38 610
150	1 820	26 050	35 220	39 750
160	20 510	27 830	36 410	40 700
170	21 870	29 540	37 500	41 490
180	23 890	31 000	38 580	42 220
190	25 230	32 430	39 490	42 850
200	26 750	33 610	40 510	43 550
210	27 080	34 800	41 200	44 100
220	29 400	35 810	41 830	44 600
230	30 650	36790	42 330	44 920
240	31 750	37 720	42 910	45 180
250	32 810	38 590	43 490	45 460
260	33 880	39 390	43 910	45 710
270	34 760	40 080	44 200	46 010
280	35 660	40 800	44 680	46 330
290	36 550	41 500	44 980	46 690
300	37 390	42 210	45 010	47 500
310	38 100	—	—	—
320	38 770	—	—	—

Table 5. Entropy of alkaline earth oxids at 273.15 °K in J/Mol °K.

MgO

Figure 4 shows Θ vs T for the low temperature region. Therein the reliability of the different methods is well visualized. The measurements are made with carbon resistances or platinum resistances; with the normal heating or continuous heating method.

The results previously obtained by BARRON et al.[7], GUNTHER[9], PARKS and KELLEY[10], GIAUQUE and ARCHIBALD[11] and the present results are plotted in Figure 5. The best known measurements, those of BARRON et al.[7] tend to be somewhat lower than

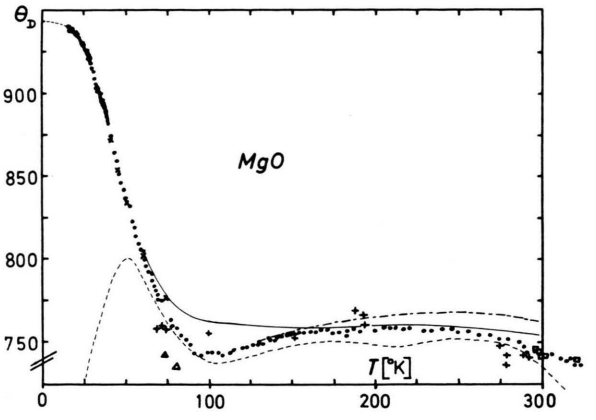

Fig. 5. Debye temperature Θ of MgO as function of T. ● ○ experimental points; ——— BARRON, BERG, MORISSON[7]; – – – – GIAUQUE, ARCHIBALD[11]; + PARKS, KELLY[10]; △ GUNTHER[9]; □ VICTOR, DOUGLAS[19]; —·— curve for Θ, calculated from the specific heat of constant volume.

the present values. The difference is at most 3% near 100 °K and 1% 300 °K. However the experimental values of DOUGLAS and VICTOR[19] — specific heat of MgO between 300 °K and 1200 °K — are near 300 °K in exellent agreement with the present results (0.5%). The differences are certainly due to the different purities of the measured specimens. The measurements of GIAUQUE and ARCHIBALD performed with very fine powder (grain size $<\mu$) show a systematic deviation to higher specific heats (up to 100% near 40 °K). This might be attributed to an effect of particle size on the specific heat[20].

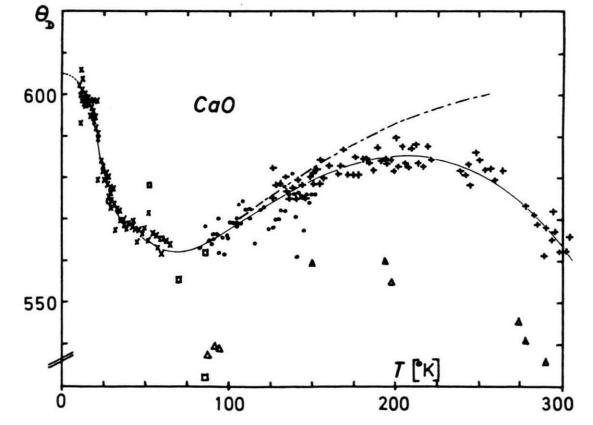

Fig. 6. Debye temperature Θ of CaO as a function of T. × · + experimental points; △ PARKS, KELLY[10]; □ NERNST, SCHWERS[12]; —·— curve for Θ, calculated from the specific heat at constant volume.

[19] TH. DOUGLAS and A. C. VICTOR, J. Res. Nat. Bur. Stand. **67 A**, 325 [1963].

[20] G. JURA and C. W. GARLAND, J. Am. Chem. Soc. **74**, 6033 [1952].

CaO (Figure 6)

The only available results for CaO, those of PARKS and KELLEY [10] and NERNST and SCHWERS [12], differ considerably from the present data. But we rember that the earlier experimental techniques provided only average values for a considerably larger temperature range. The different experimental curves for CaO have been obtained with an intervall of about 1 year.

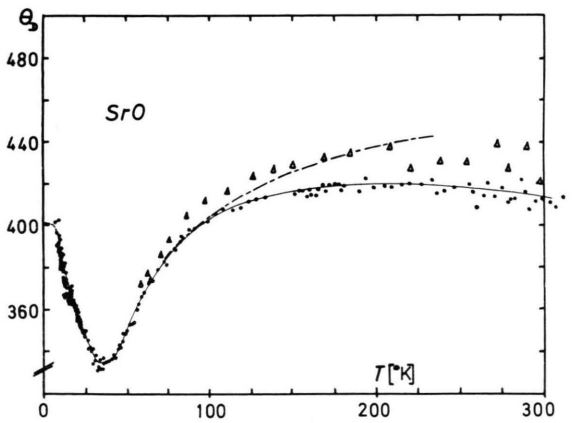

Fig. 7. Debye temperature Θ of SrO as a function of T. ● experimental points; △ ANDERSON [13]; —·— curve for Θ, calculated for the specific heat at constant volume.

SrO and BaO (Figures 7 and 8)

The experimental data for BaO agree very well with the previous work of ANDERSON [13] within the experimental errors. However the agreement is less

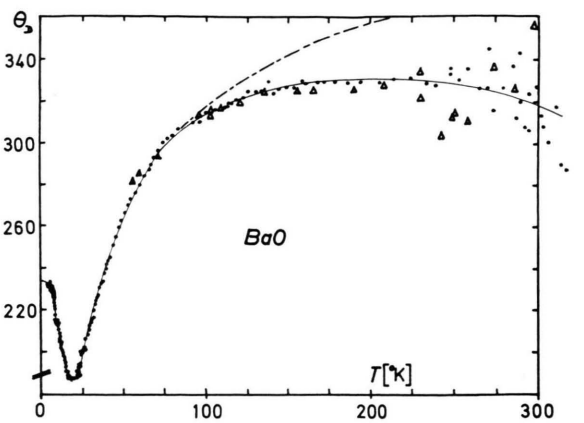

Fig. 8. Debye temperature Θ of BaO as a function of T. ● experimental points; △ ANDERSON [13]; —·— curve for Θ, calculated for the specific heat at constant volume.

for SrO ,where the present data of the specific heat are at least 2 to 4% higher between 100 and 300 °K. The different sample purities could provide again the observed differences.

Other thermal properties of these crystals and the comparison of these results with the existing lattice theories are fully described in part II.

Acknowledgement

The author expresses his sincere thanks to Professor L. WEIL for his interest and encouragement in beginning this work, to Dr. S. VIEIRA for his assistance in part of the measurements and some helpful conversations; to M. VITTER for the MgO-sample preparation and to Miss E. NEDELKA for her kind help in preparing the computer calculation programmes.