The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part IV. Evaluation of its specific heat

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1. Introduction

Einstein's classic paper of 1907 introducing his theory of specific heats was based on an application of the fundamental notions of the quantum theory and of thermodynamics to the problem of determining the thermal behaviour of a body assumed to be constituted of a great number of structural elements, each of which is an oscillator having a definite frequency of vibration. Basing himself on the assumption that their energy of vibration obeys the quantum rules, Einstein obtained an expression for the total vibrational energy of the body, in other words for its heat content, in terms of the frequency or frequencies of vibration of the oscillators, their numbers and the absolute temperature. Einstein's theory and its results may be summed up by the statement that the thermal energy content of a substance is determined by the vibration spectrum of the elementary structures of which it is constituted.

A well known theorem in classical mechanics states that the small vibrations of a system of particles result from the superposition of a set of normal modes, in each of which the particles of the system vibrate with the same frequency and in the same or opposite phases, the total number of normal modes being the same as the number of degrees of dynamic freedom of the system. The normal modes in the sense of this theorem which the structure of a crystal can exhibit may be readily deduced. The argument is the same as that used earlier in part II of this memoir for the particular case of the MgO structure. If each unit cell of the crystal contains p atoms, the crystal has $(24p - 3)$ species of normal modes; this number is the same as the degrees of dynamic freedom of the group of $8p$ atoms included in a volume element of which the dimensions are twice as large as those of the unit cell; the three omitted modes are the translatory movements of the group.

In the earlier parts of this memoir it has been shown that the 45 species of normal modes indicated by the general theory for MgO ($p = 2$) reduce to nine only by reason of the cubic symmetry of the crystal. These nine modes were

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Table 1. Normal modes and frequencies

Description of the mode	Degeneracy	Frequency in cm^{-1}
Oscillation of the Mg and O atoms in the unit cells in opposite phases	3	490 obs.
Normal oscillation of the O atoms in the octahedral planes	4	463 obs.
Tangential oscillation of the O atoms in the octahedral planes	8	446 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in opposite phases	6	423 obs.
Normal oscillation of the Mg atoms in the octahedral planes	4	400 obs.
Tangential oscillation of the Mg atoms in the octahedral planes	8	387 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in the same phase	3	365 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in opposite phases	3	313 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in the same phase	6	277 obs.
Continuous spectrum	3	277 → 0

described and their activity in the absorption and reflection of infra-red radiation was discussed. It emerged that the theory accounts in a highly satisfactory and comprehensive fashion for the observed spectroscopic properties of MgO.

We shall now proceed to show that the thermal energy content of the MgO crystal and its variation with temperature can be fully worked out on the basis of the same theory as its spectroscopic behaviour. We shall make use of the original ideas of Einstein and the spectroscopic data derived from our experimental studies. The specific heat of MgO and its variation with temperature thus deduced are found to be in complete agreement with the experimental data reported in the literature. It is significant that no use whatever is made of data regarding any other properties of MgO in this connection. The power and validity of the present approach to specific heat theory are thus demonstrated.

2. The vibrational spectrum of MgO

Table 1 given above is self-explanatory. It assembles the relevant particulars set out and discussed in the preceding parts of the memoir. The total of the degeneracies listed in the second column of the table is 48, which is also the number of degrees of dynamic freedom of a group of 8 O atoms and 8 Mg atoms which forms the dynamic unit in the crystal structure. The number of such groups

is one-eighth of the number of MgO "molecules" present in the crystal. This 16-atom group is the oscillator with which we are concerned in specific heat theory. Forty-five out of its 48 degrees of freedom are manifested as the discrete frequencies listed in the third column of the table. The remaining three degrees of freedom are the translations of the oscillator. They appear as the last entry of the table and are there described as a continuous spectrum with a degeneracy 3 and ranging in frequency from $277\,\mathrm{cm}^{-1}$ down to zero. The justification for these entries will appear later.

To determine the contributions to the molecular heat of the modes with discrete frequencies shown in the third column of table 1 we use the available tabulations of the Einstein specific heat function and find its value for the particular frequency at the particular temperature under consideration. *Twice the value of the Einstein function multiplied by the degeneracy of the mode and divided by 48 gives the contribution of the mode to the molecular heat of MgO.* Proceeding in this fashion for all the nine frequencies we can sum up the results obtained. Dividing the total obtained by 40·32 which is the molecular weight of MgO, we obtain a tabulation of the specific heat of MgO as a function of the temperature, in so far as it arises from the spectrum of vibrations with discrete frequencies.

In the general case of a crystal containing p atoms in each unit cell, the $(24p - 3)$ normal modes of vibration account for all the degrees of freedom of movement of the group of $8p$ atoms which is the oscillator in specific heat theory except for the three degrees which represent its translations. Even in the case of the crystals with the simplest structure $(p = 1)$ these translations take up only three out of every 24 degrees of freedom. When $p = 2$, as in the case of MgO, the translations represent only three out of 48 degrees of freedom. In the case of more complex crystals they form an even smaller proportion of the whole. Nevertheless, the movements within the crystal which they represent and the contributions which these make to the thermal energy cannot be ignored. We shall now proceed to consider these matters.

3. The residual spectrum

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very

low values. In other words, the vibration spectrum of MgO with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

Consider two sets of volume elements whose linear dimensions are respectively m and n times greater than those of the atomic groups which we have recognised as the dynamic units of crystal structure. The number of such volume elements would be respectively $1/m^3$ and $1/n^3$ times smaller than the number N in the crystal of atomic groups referred to. Let v_m and v_n be respectively the lowest frequencies of internal vibration of these volume elements. We may reasonably assume that the vibration frequencies are inversely proportional to the linear dimensions of the oscillators. We may accordingly write $v_m = f/m$ and $v_n = f/n$, where f is a constant having the dimensions of a frequency. In the limit when m approaches n, we may write $v_m - v_n = dv$. The number of oscillators whose frequencies lie within the range dv would be thrice the difference in the number of volume elements whose lowest frequencies are respectively v_m and v_n, and is thus the same as $3N(1/m^3 - 1/n^3)$ in the limit where m approaches n. We may write this difference as $9Nv^2 dv/f^3$. Integrating it over the whole frequency range covered by the residual spectrum, we should regain the number $3N$. We are thereby enabled to identify the constant f with the upper frequency limit v_L of the residual spectrum. The vibrational modes are thus distributed in the residual spectrum in the manner defined by the function $9Nv^2 dv/v_L^3$.

Thus, to find the contribution to the thermal energy of the crystal arising from the residual spectrum of vibrations, we multiply the average energy of an oscillator of frequency v as given by Einstein's theory by the number of such oscillators distributed over its range of frequency as deduced above and integrate the product between the limits v_L and zero. The contribution to the specific heat would then be the differential of the energy thus evaluated with respect to temperature. The functions which come up for computation in this procedure are well known and as tabulations of them are available, it is a simple matter to find the contributions to the specific heat of MgO arising from the residual spectrum at various temperatures. These are then added to the contributions of the Einstein terms arising from the nine discrete frequencies of the lattice at the respective temperatures. The upper limit v_L of the frequency range covered by the residual spectrum in this evaluation is necessarily the lowest of the nine discrete frequencies of MgO, viz., 277 cm^{-1}. The contribution of the residual spectrum to the specific heat at different temperatures evaluated in this manner has been entered in tables 2, 3 and 4 as the last entry 3D(277) after the contribution of the

Table 2. Computation of specific heat

	50° K	75° K	100° K	125° K	150° K	175° K	200° K	225° K
3E(490)	0·0001	0·0049	0·0300	0·0805	0·1465	0·2163	0·2824	0·3414
4E(463)	0·0002	0·0100	0·0529	0·1315	0·2281	0·3254	0·4144	0·4921
8E(446)	0·0007	0·0255	0·1258	0·2984	0·5016	0·7003	0·8789	1·0325
6E(423)	0·0010	0·0269	0·1189	0·2643	0·4258	0·5784	0·7114	0·8240
4E(400)	0·0011	0·0252	0·0993	0·2069	0·3202	0·4228	0·5105	0·5830
8E(387)	0·0031	0·0605	0·2253	0·4525	0·6841	0·8900	1·0629	1·2049
3E(365)	0·0020	0·0310	0·1038	0·1965	0·2858	0·3625	0·4255	0·4764
3E(313)	0·0067	0·0629	0·1649	0·2715	0·3624	0·4347	0·4909	0·5342
6E(277)	0·0302	0·1993	0·4432	0·6653	0·8405	0·9729	1·0717	1·1463
3D(277)	0·1003	0·2420	0·3700	0·4647	0·5315	0·5787	0·6125	0·6372
Mol. heat	0·1454	0·6882	1·7341	3·0321	4·3265	5·4820	6·4611	7·2720
Sp. heat	0·0036	0·0171	0·0430	0·0752	0·1073	0·1360	0·1602	0·1804

Table 3. Computation of specific heat

	250° K	275° K	300° K	350° K	400° K	450° K	500° K
3E(490)	0·3926	0·4364	0·4736	0·5321	0·5746	0·6059	0·6297
4E(463)	0·5586	0·6146	0·6616	0·7346	0·7870	0·8258	0·8547
8E(446)	1·1620	1·2708	1·3612	1·5007	1·6000	1·6731	1·7283
6E(423)	0·9178	0·9952	1·0591	1·1568	1·2259	1·2764	1·3122
4E(400)	0·6428	0·6913	0·7313	0·7916	0·8336	0·8648	0·8869
8E(387)	1·3205	1·4146	1·4906	1·6059	1·6867	1·7429	1·7892
3E(365)	0·5171	0·5500	0·5765	0·6163	0·6439	0·6627	0·6790
3E(313)	0·5680	0·5946	0·6161	0·6475	0·6690	0·6841	0·6949
6E(277)	1·2035	1·2481	1·2832	1·3340	1·3692	1·3929	1·4109
3D(277)	0·6558	0·6700	0·6811	0·6971	0·7079	0·7154	0·7208
Mol. heat	7·9387	8·4850	8·9343	9·6166	10·0978	10·4440	10·7066
Sp. heat	0·1969	0·2104	0·2216	0·2385	0·2504	0·2590	0·2655

discrete frequencies. The latter are determined from the respective Einstein functions and are indicated in these tables as 3E(490), 4E(463), etc.

4. Comparison with the measured specific heats

The specific heat of MgO has been the subject of experimental determination by several investigators over different ranges of temperature. Their data have been collected and put together in the form of a table at convenient intervals of

Table 4. Computation of specific heat

	550° K	600° K	650° K	700° K	750° K	800° K	850° K
3E(490)	0·6483	0·6615	0·6754	0·6835	0·6906	0·6969	0·7022
4E(463)	0·8757	0·8952	0·9088	0·9191	0·9282	0·9358	0·9423
8E(446)	1·7673	1·8054	1·8281	1·8482	1·8652	1·8799	1·8915
6E(423)	1·3440	1·3653	1·3821	1·3961	1·4079	1·4176	1·4255
4E(400)	0·9058	0·9180	0·9286	0·9371	0·9442	0·9500	0·9547
8E(387)	1·8210	1·8451	1·8649	1·8815	1·8943	1·9053	1·9141
3E(365)	0·6890	0·6975	0·7044	0·7097	0·7141	0·7176	0·7207
3E(313)	0·7033	0·7097	0·7144	0·7187	0·7221	0·7247	0·7269
6E(277)	1·4239	1·4340	1·4421	1·4486	1·4536	1·4581	1·4616
3D(277)	0·7247	0·7279	0·7303	0·7323	0·7338	0·7352	0·7362
Mol. heat	10·9030	11·0596	11·1791	11·2748	11·3540	11·4211	11·4757
Sp. heat	0·2704	0·2743	0·2773	0·2796	0·2816	0·2833	0·2846

Table 5. Measured specific heats of MgO

Absolute temperature	53°	73°	93°	123°	173°	223°
Specific heat	0·0033	0·0158	0·0358	0·0741	0·1290	0·1768
Absolute temperature	273°	323°	373°	473°	673°	873°
Specific heat	0·2078	0·2317	0·2437	0·2604	0·2771	0·2915

temperature in the *International Critical Tables* (Vol. V, 1929, page 98). They are reproduced in table 5 after conversion from joules to calories.

A comparison of the figures appearing in table 5 with the calculated specific heats at the nearest temperatures appearing in tables 2, 3 and 4 shows that the variation of specific heat with temperature as actually measured is well represented by the theoretical computations. The excellence of the agreement is made clearer in figure 1 where the theoretical curve is drawn as a continuous line while the dots represent the experimental data.

At the lowest temperature of 50° K listed in table 2, the contribution of the residual spectrum to the specific heat forms the largest part of the whole. But as the temperature rises, its relative importance diminishes rapidly, being only 1/5th of the whole at 100° K and 1/10th at 200° K. It thereafter diminishes progressively to its limiting value of 1/16th. These changes are a consequence of the continued increase with rising temperature of the contributions of the discrete frequencies to the specific heat, while on the other hand, the contribution of the residual spectrum soon reaches its limiting value. It will be noticed from tables 2 and 3 that E(277) and D(277) become nearly equal to each other at temperatures higher
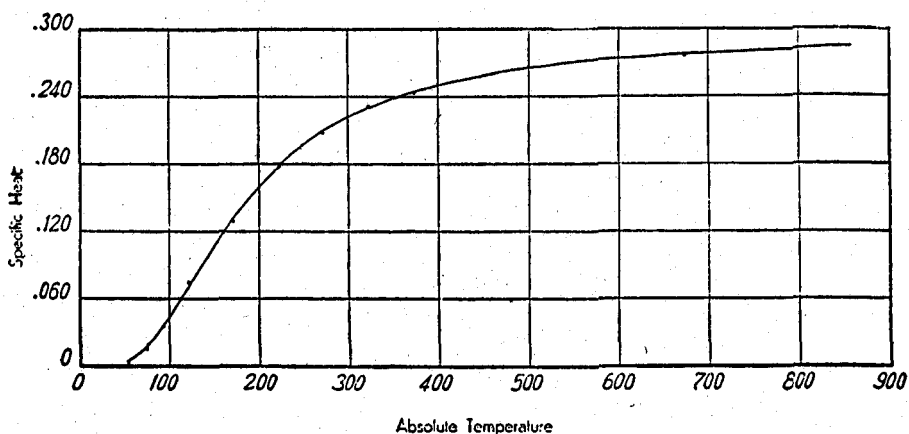
Figure 1. Specific heat of MgO. Calculated————. Observed ● ● ● ●.

than 250° absolute. This is a consequence of the fact that the vibrational modes appearing in the residual spectrum are clustered near its upper limit of frequency. This is equivalent to stating that the residual spectrum arises for the most part from internal oscillations in volume elements whose dimensions are not very much larger than those of the dynamic units in the crystal. A great majority of them may be about four times as large in each direction as the unit cells of the crystal structure. Only at the very lowest temperatures, when the modes of higher frequencies cease to be excited, would any appreciable part of the thermal energy be ascribable to oscillators of still larger sizes.

5. Summary

The specific heat of MgO at various temperatures from 50 to 850° absolute is computed by adding up the Einstein functions corresponding to the nine modes with discrete frequencies indicated by the dynamical theory and confirmed by infra-red spectroscopy. To this is added the contribution from a residual spectrum of vibrations of lower frequencies, the existence of which is also indicated by the dynamical theory. A very satisfactory agreement emerges over the whole range of temperatures between the calculated and observed specific heats.