The spectroscopic behaviour of rock-salt and the evaluation of its specific heat—Part IV. Specific heat and spectral frequencies

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1. Introduction

The numerous published measurements of the thermal energy-content of crystalline solids and its variation with temperature make it clear that the theory of specific heats is concerned with the movements of the atomic nuclei in crystals about their positions of equilibrium and especially with the frequencies of their vibrations. A clear picture of the nature of these vibrations emerges if we take the basic facts of crystal architecture as our starting point, viz., that a crystal consists of an immense number of similar and similarly situated units of structure. Each unit of structure contains a group of atomic nuclei which can interact with each other through the electrons which hold them together. The next step is to make use of the theory of small vibrations in classical mechanics to find the normal modes and frequencies of free vibration of these nuclei about their positions of equilibrium. In treating this problem, we have of necessity to recognise and take account of the three-dimensional periodicity of the crystal architecture. The principles of thermodynamics and of the quantum theory have then to be introduced and applied to the problem. They indicate that the normal modes deduced classically would be excited to various levels of energy, the relative probabilities of such excitation being determined by the respective energies and the absolute temperature. The average energy associated with each such normal mode and hence also the total average energy of all the normal modes taken together can then be computed. A multiplication of this average by the number of the oscillators in the crystal considered gives the total thermal energy of the solid as a function of the temperature.

It has been shown in the preceding parts of this memoir that a basically similar approach enables us to explain or elucidate the spectroscopic properties of the crystal. It follows that the thermal and spectroscopic behaviours of the crystal stand in the closest relationship to each other. It should therefore be possible by

making use of the spectroscopically determined frequencies of vibration to evalute the specific heat of the crystal as a function of temperature and proceed to a comparison of the results thus obtained with the measured specific heats. No data are required for such an evaluation except those emerging from the spectroscopic studies. It follows that an agreement between theory and experiment would constitute a perfect demonstration of the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.

2. The spectral frequencies of rock-salt

In the case of magnesium oxide which has been dealt with in memoir No. 127 appearing in the same issue of these *Proceedings*, the spectroscopic frequencies were determined by the study of infra-red absorption in that crystal. In the case of rock-salt now considered, we have two distinct methods of investigation available which, as has already been noticed, give results supporting each other and confirming the inferences from theory. Of the two methods of study, viz.,
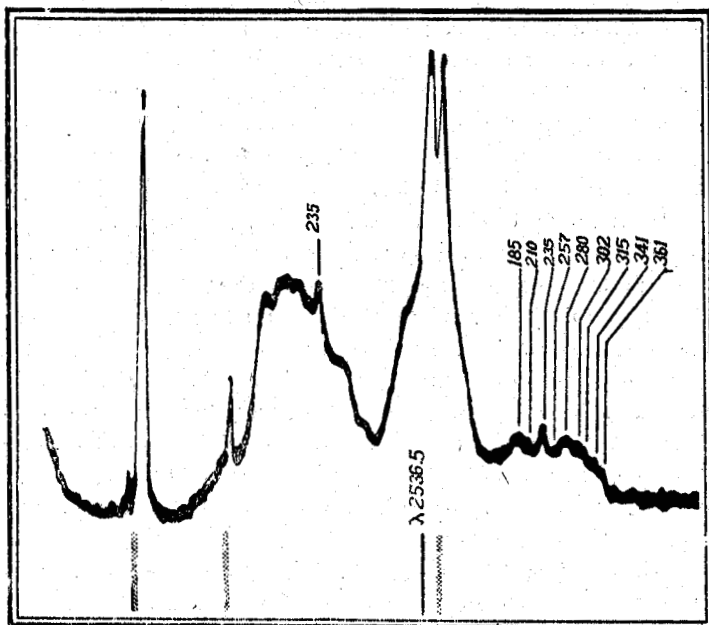

Figure 1. Microphotometer record showing frequency shifts.

infra-red spectroscopy and the scattering of light, the latter is definitely superior, since the data furnished by it are both complete and exact. All the nine modes appear in light-scattering with doubled frequency shifts with respect to the position in the spectrum of the $\lambda 2536\cdot5$ radiation of the mercury arc used to illuminate the crystal. The spectral shifts are recorded on both sides of the exciting radiation, and the microphotometer records of the spectrum on the two sides usefully supplement each other. On the heavily exposed side, the background due to the continuous radiation in the incident light is relatively less important, and the record therefore gives a truer picture of the spectrum taken as a whole. But, on the other hand, the heavy exposure results in obscuring finer detail and its microphotometer record fails to exhibit a complete resolution of the spectrum into its distinct components. The microphotometric record of the weakly exposed side is greatly superior in this respect. Not only does it reveal the nine distinct double-frequency shifts in the scattered light but also enables them to be read off directly from the record with tolerable accuracy.

Figure 1 in the text is the same record as that reproduced as figure 1 in the previous part of the memoir. But now the frequency shifts have been entered and shown against the visible peaks in the record which enabled them to be measured with reference to the position of the exciting radiation, the prominent $235\,\mathrm{cm}^{-1}$ shift being used to furnish the necessary scale of frequencies. The frequency shifts determined in this manner and entered in the figure differ little from those obtained by measurements under a micrometer of original spectrum plates recorded with rock-salt.

3. Comparison with the specific heat data

Ther manner in which we proceed from the spectroscopic frequencies to evaluate the specific heat of rock-salt as a function of the temperature is entirely analogous to that already fully explained for the case of MgO in a memoir appearing in the same issue of these *Proceedings*. It is unnecessary to traverse the ground here once again and it suffices to present a tabulation of the contributions to the specific heat made by the different normal modes of vibration, as also by the residual spectrum of vibration frequencies which is continuous and extends towards zero frequency. The normal frequencies of vibration made use of in the calculations are one-half the frequency shifts (in cm^{-1}) observed in the scattering of light.

Though the structure of rock-salt is similar to that of MgO, the two cases differ in certain important respects. The vibration spectrum of rock-salt lies much further out in the infra-red than that of MgO. As is to be expected in the circumstances, the increase in its specific heat from very low to normal values takes place for the most part in the region of liquid air and liquid hydrogen temperatures. Tabulations are therefore required in the case of rock-salt only for temperatures between 0 and 300 degrees absolute.
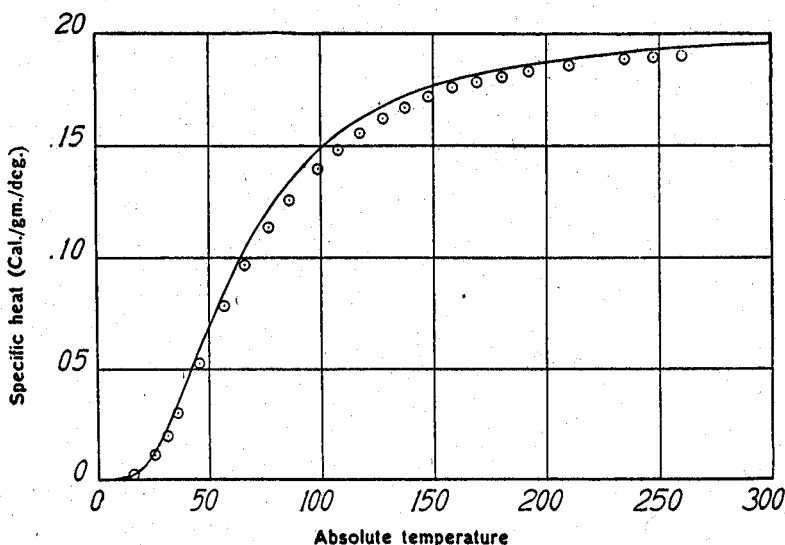
Figure 2. Comparison of theory and experiment. Theory——————. Experiment ⊙ ⊙ ⊙.

The foregoing remarks have some further implications. As has been pointed out in the third part of this memoir, the frequency shifts observed in light scattering exhibit a temperature effect. The frequency shifts broaden asymmetrically and also move to smaller values as the temperature is raised. In the case of rock-salt, the spectroscopic data we make use of were obtained with the crystal held at room temperature. Hence, it cannot be expected that these data would fit the specific heat curve at very low temperatures and especially at the temperatures where the specific heat changes most rapidly. We could only expect the theoretically calculated specific heats for low temperatures to agree with observed specific heats if the frequencies used had been determined with the crystal held at the same temperatures.

The foregoing remarks find support in the results of the actual computations. Tables 1 and 2 show the specific heats as computed and the results have been drawn as a continuous graph in figure 2 in the text. The experimental values in the same range of temperatures are given in table 5 and have been shown as dotted circles in figure 2. It will be seen that the experimental values lie systematically below the theoretical curve, the deviations being greatest in the range between 50 and 150 degrees absolute.

The differences between theory and experiment indicated in figure 2 arise, without doubt, by reason of the spectroscopic frequencies used in the calculations being less than the actual spectroscopic frequencies at low temperatures. Precisely what the latter are cannot be stated on the basis of present knowledge.

Table 1. Computation of the specific heats

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
$3E_1(180\,cm^{-1})$	—	—	0·0023	0·1088	0·2929	0·4312	0·5223
$4E_2(170\,cm^{-1})$	—	—	0·0047	0·1738	0·4278	0·6091	0·7235
$8E_3(157\,cm^{-1})$	—	0·0001	0·0176	0·4359	0·9638	1·3059	1·5135
$6E_4(150\,cm^{-1})$	—	0·0001	0·0181	0·3673	0·7652	1·0137	1·1610
$4E_5(140\,cm^{-1})$	—	0·0002	0·0188	0·2876	0·5545	0·7099	0·7994
$3E_6(129\,cm^{-1})$	—	0·0004	0·0226	0·2571	0·4517	0·5593	0·6180
$8E_7(118\,cm^{-1})$	—	0·0026	0·0960	0·8042	1·3013	1·5608	1·6985
$3E_8(110\,cm^{-1})$	—	0·0019	0·0502	0·3362	0·5154	0·6043	0·6506
$6E_9(92\,cm^{-1})$	0·0004	0·0156	0·2056	0·8453	1·1482	1·2852	1·3569
$3D(92\,cm^{-1})$	0·0240	0·0767	0·2458	0·5332	0·6378	0·6818	0·7036
Molecular heat (cal/gm/deg)	0·0244	0·0976	0·6817	4·1494	7·0586	8·7612	9·7473
Specific heat (cal/gm/deg)	0·0004	0·0017	0·0117	0·0710	0·1208	0·1499	0·1668

Table 2. Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
$3E_1(180\,cm^{-1})$	0·5805	0·6195	0·6468	0·6647	0·6805	0·6909	0·6983
$4E_2(170\,cm^{-1})$	0·7952	0·8416	0·8738	0·9005	0·9156	0·9283	0·9377
$8E_3(157\,cm^{-1})$	1·6398	1·7249	1·7807	1·8229	1·8510	1·8753	1·8927
$6E_4(150\,cm^{-1})$	1·2507	1·3084	1·3528	1·3776	1·3965	1·4125	1·4248
$4E_5(140\,cm^{-1})$	0·8530	0·8863	0·9114	0·9269	0·9390	0·9487	0·9554
$3E_6(129\,cm^{-1})$	0·6542	0·6774	0·6920	0·7023	0·7106	0·7166	0·7204
$8E_7(118\,cm^{-1})$	1·7807	1·8340	1·8673	1·8903	1·9087	1·9211	1·9326
$3E_8(110\,cm^{-1})$	0·6785	0·6941	0·7063	0·7141	0·7197	0·7241	0·7274
$6E_9(92\,cm^{-1})$	1·3945	1·4178	1·4347	1·4455	1·4535	1·4599	1·4644
$3D(92\,cm^{-1})$	0·7159	0·7229	0·7281	0·7314	0·7338	0·7357	0·7370
Molecular heat	10·3430	10·7269	10·9939	11·1762	11·3089	11·4131	11·4907
Specific heat (cal/gm/deg)	0·1770	0·1835	0·1881	0·1912	0·1935	0·1953	0·1966

Any attempt to fit theory and experiment by using assumed values for the frequencies might well be thought artificial and unsatisfactory. It appeared however useful to present a second set of computations in which all the frequencies made use of are raised uniformly by 5% of their respective values. Such an increase is certainly not greater than would be justified by a comparison with those cases, e.g., quartz and calcite, where the effect of using liquid air temperatures on the vibration frequencies has been quantitatively studied. The fresh computations on this basis have been shown in tables 3 and 4, and their

Table 3. Computation of the specific heats

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
$3E_1$(189 cm^{-1})	—	—	0·0015	0·0925	0·2678	0·4058	0·5034
$4E_2$(179 cm^{-1})	—	—	0·0031	0·1478	0·3944	0·5794	0·6986
$8E_3$(165 cm^{-1})	—	0·0001	0·0121	0·3804	0·8966	1·2504	1·4693
$6E_4$(158 cm^{-1})	—	0·0001	0·0125	0·3212	0·7165	0·9725	1·1318
$4E_5$(147 cm^{-1})	—	0·0001	0·0138	0·2576	0·5233	0·6872	0·7804
$3E_6$(135 cm^{-1})	—	0·0002	0·0175	0·2339	0·4312	0·5443	0·6073
$8E_7$(124 cm^{-1})	—	0·0017	0·0749	0·7360	1·2504	1·5223	1·6715
$3E_8$(116 cm^{-1})	—	0·0012	0·0392	0·3104	0·4949	0·5901	0·6412
$6E_9$(97 cm^{-1})	0·0002	0·0106	0·1674	0·7949	1·1153	1·2624	1·3416
$3D$(97 cm^{-1})	0·0204	0·0665	0·2213	0·5146	0·6270	0·6746	0·6991
Molecular heat	0·0206	0·0805	0·5633	3·7893	6·7174	8·4890	9·5442
Specific heat (cal/gm/deg)	0·0004	0·0014	0·0096	0·0648	0·1149	0·1452	0·1633

Table 4. Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
$3E_1$(189 cm^{-1})	0·5659	0·6073	0·6370	0·6566	0·6754	0·6856	0·6941
$4E_2$(179 cm^{-1})	0·7761	0·8280	0·8625	0·8883	0·9087	0·9213	0·9323
$8E_3$(165 cm^{-1})	1·6113	1·6985	1·7603	1·8092	1·8397	1·8620	1·8833
$6E_4$(158 cm^{-1})	1·2268	1·2909	1·3355	1·3672	1·3883	1·4045	1·4178
$4E_5$(147 cm^{-1})	0·8397	0·8754	0·9046	0·9213	0·9337	0·9440	0·9522
$3E_6$(135 cm^{-1})	0·6468	0·6708	0·6878	0·6983	0·7071	0·7133	0·7181
$8E_7$(124 cm^{-1})	1·7572	1·8201	1·8567	1·8833	1·9020	1·9149	1·9273
$3E_8$(116 cm^{-1})	0·6708	0·6888	0·7013	0·7106	0·7166	0·7212	0·7254
$6E_9$(97 cm^{-1})	1·3840	1·4105	1·4283	1·4409	1·4495	1·4574	1·4621
$3D$(97 cm^{-1})	0·7126	0·7207	0·7261	0·7300	0·7326	0·7350	0·7364
Molecular heat	10·1912	10·6110	10·9001	11·1057	11·2536	11·3592	11·4490
Specific heat (cal/gm/deg)	0·1744	0·1815	0·1865	0·1900	0·1925	0·1943	0·1959

results plotted in figure 3 against the experimental results. The greatly improved agreement between theory and experiment which is exhibited in figure 3 makes it clear that the lack of such agreement appearing in figure 2 is due to the frequencies made use of in that case not being the actual frequencies. Indeed, a perfect fit with the experimental data could have been obtained by appropriate alterations in the frequencies made use of in the calculations. But it did not appear worthwhile to attempt to do this for the reason that figures 2 and 3 by themselves make it perfectly clear that the approach to the specific heat theory made in the present investigation is essentially a complete success.

Table 5. Experimental data of specific heats

Temperature	10·9° K	15·3° K	25·1° K	50·7° K	76·4° K	103·1° K
Molecular heat	0·044	0·134	0·658	3·820	6·626	8·424
Specific heat (cal/gm/deg)	0·0008	0·0023	0·0113	0·0654	0·1134	0·1441

Temperature	127·7° K	153·2° K	174·9° K	198·1° K	222·5° K	253·9° K	260·6° K
Molecular heat	9·486	10·162	10·542	10·792	11·006	11·104	11·134
Specific heat (cal/gm/deg)	0·1623	0·1739	0·1804	0·1846	0·1883	0·1900	0·1905

Experimental values of specific heat of NaCl taken from K Clusius, J Goldmann and A Perlick, Z. *Naturforsch.*, A4, 424–432 (1949).
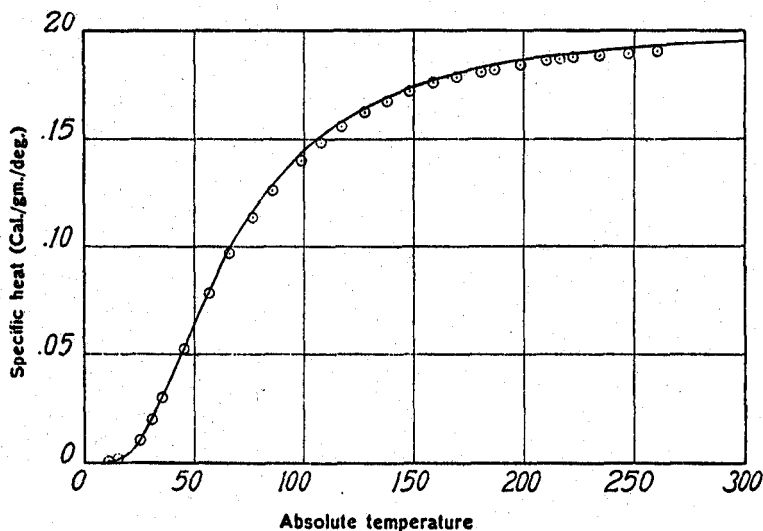

Figure 3. Comparison of theory and experiment. Theory————. Experiment ⊙ ⊙ ⊙.

4. Summary

The spectroscopically determined vibration frequencies of the rock-salt structure are made use of for a theoretical evaluation of its specific heat as a function of

temperature. The results thus obtained are compared with the measured specific heats. The agreement between theory and experiment which emerges demonstrates the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.