The specific heats of the alkali halides and their spectroscopic behaviour—Part VII. Evaluation of the specific heats

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In seeking to evaluate the thermal energy of a crystal on the basis of the principles of thermodynamics and of the quantum theory, we have to find answers to the following questions: What are the oscillators of which the vibrational energies need to be quantised and totalled up? How can they be identified and enumerated? We shall presently see that the treatment of the problem of the modes of atomic vibration given in the earlier parts of the memoir itself provides the answers to these questions.

We may begin with the case of a simple Bravais lattice. Since each atom in the lattice has 3 degrees of freedom, the general principle that equivalent atoms have the same amplitude while their phases of vibration are either the same or else alternate along one or two or all three axes, results in a simple lattice having 24 possible kinds of movement. Of these, 21 have the character of normal modes of vibration, while the three others are simple translations. In the particular case of a face-centred cubic lattice, the unit cell is a rhombohedron. The total number of degrees of dynamic freedom of movement of the eight atoms located at the corners of this rhombohedron is also 24. Thus, the 21 modes of vibration of the lattice may also be considered as normal modes of vibration of this 8-atom group and its 3 translations as movements of the entire group.

We have seen that the alkali halide structure has nine distinct frequencies of vibration of which the degeneracies are respectively 3, 6, 3, 4, 8, 4, 8, 3 and 6. These add up to a total of 45, or if we include the three omitted translations, to 48. A sixteen-atom group consisting of eight metal and eight halogen atoms linked to each other by chemical bonds would also have 48 degrees of dynamic freedom of movement. Hence, we may appropriately regard such a group as the dynamic unit in the crystal and its nine distinct frequencies of vibration with their characteristic degeneracies as "oscillators" in the specific-heat theory. The three omitted degrees of freedom would be the three translations of the 16-atom group.

It should be remarked that the two cases considered above are only particular examples of a general theorem applicable to all crystals. As has been shown

earlier, if the unit cell of a crystal contains n non-equivalent atoms, the structure of the crystal has $(24n - 3)$ normal modes of vibration. In $(3n - 3)$ of these modes, the vibrations appear in adjacent cells of the lattice with the same amplitudes and phases, while in the $21n$ other modes, the amplitudes of vibration are the same for equivalent atoms but their phases alternate along one, two, or all three axes of the structure. Hence, the *dynamic* unit in the crystal has twice the linear dimensions and hence eight times the volume of the unit cell of its structure. It, therefore, contains $8n$ atoms. The total number of degrees of dynamic freedom of these $8n$ atoms is $24n$. Accordingly, we may describe the $(24n - 3)$ normal modes of vibration of which the structure is capable as the *internal* modes of vibration of the group of $8n$ atoms, while the 3 degrees of freedom not thus accounted for would be the three translations of the group. Thus, the group of $8n$ atoms, or rather each of its frequencies of internal vibration, is identified as the unit oscillator in specific-heat theory, each frequency being counted as many times over as the degeneracy which it may exhibit by reason of the symmetry of the crystal.

One can readily understand why the dynamic unit has twice the linear dimensions and therefore eight times the volume of the static unit in the structure of a crystal. In any normal mode, the vibrations in any one cell would necessarily be coupled with the vibrations in the adjacent cells. In such coupled vibrations, the phases of the vibration in adjacent cells along each axis of the structure may be either the same or opposite. There would thus be eight different possibilities and the vibration frequencies in each of them would necessarily be different. This is the same result as that stated above.

Leaving aside for a moment the translatory movements of the 16-atom groups, we shall consider their internal vibrations. These vibrations appear in the infrared region of the spectrum and the interatomic forces which determine their frequencies are necessarily strong. But they operate only at short ranges and it may be assumed that they are negligible as between atoms which are further apart from each other than the dimensions of the 16-atom groups. In these circumstances, the internal vibrations of these groups excited by the thermal agitation in the crystal may be expected to be uncorrelated, in other words, to exhibit no coherent relationships of phase as between the different groups. We are accordingly justified in the specific-heat problem in regarding the 16-atom groups as independent oscillators and quantising their energies on that basis.

The thermal energy of the crystal is a summation of the quantised energies of the oscillators of different frequencies included in its volume. There are nine distinct frequencies of vibration, and the number of oscillators having a particular frequency is the same as the number of 16-atom groups contained in the crystal multiplied by the degeneracy of the particular mode. It follows that the Einstein specific-heat function for the particular frequency multiplied by the degeneracy of the mode and divided by 48 gives the contribution of all the oscillators having that frequency to the atomic heat of the crystal. Summing up the contributions

thus made by all the nine frequencies, we obtain the atomic heat of the crystal as a function of the temperature so far as it arises from the spectrum of internal vibrations with discrete frequencies.

We have now to ascertain the contributions to the thermal energy arising from the three translatory movements of the 16-atom groups which we have so far ignored. These translations would necessarily result in displacing the neighbouring atomic groups and hence would set up forces resisting the movement. It follows that the degrees of freedom which do not appear as internal vibrations of the 16-atom groups would manifest themselves as the internal vibrations of atomic groups of larger dimensions. The larger such groups are, the lower would be their possible frequencies of vibration. Hence, the thermal agitation in the crystal associated with the vibrations of specific frequencies already considered would be accompanied by a residual spectrum which by the very nature of the case cannot be expected to exhibit any discrete frequencies and may accordingly be assumed to be continuous and to extend down to very low frequencies.

If the number of 16-atom groups included in the volume of the crystal is N, the total number of degrees of freedom manifested in the residual spectrum would be 3N. The manner in which the 3N degrees are distributed over the range of frequencies covered by that spectrum can be determined by statistical considerations of an elementary nature. We base ourselves on the very reasonable assumption that the lowest frequency of vibration of an atomic group which we denote by v is inversely proportional to the linear dimensions of the group. On this basis, the volume of each group would be inversely proportional to v^3. Consequently, the number of such groups included in the crystal would be directly proportional to v^3. Hence, the number of degrees of freedom manifested in the spectral range between v and $v + dv$ would be proportional to its differential, viz., $3v^2 dv$. We assume the spectrum to extend between the lower limit 0 and an upper limit v_L. Since the total number of degrees of freedom obtained by integration over this range should be 3N, we obtain the law of distribution to be $3N \cdot 3v^2 dv / v_L^3$. Multiplying this by the Einstein specific-heat function and integrating the product between the limits 0 and v_L and dividing by 48, we obtain the contribution of the residual spectrum to the atomic heat of the crystal.

Since the residual spectrum represents the frequencies of internal vibration of atomic groups whose dimensions are larger than those of the 16-atom group, v_L should be of the same order of magnitude as the lowest of its nine discrete frequencies of vibration. We shall not, therefore, be far wrong, at least in the case of the alkali halides, in taking v_L to be equal to the lowest of the nine discrete frequencies.

Of the total number of degrees of atomic freedom, only one-sixteenth part appears in the residual spectrum of frequencies. The largest part of this again is concentrated near the upper limit of that spectrum by reason of the law of distribution of frequencies in it. Indeed, only 1/128th part of the total number of degrees of atomic freedom would be left not accounted for if we omitted to

consider vibrations in volume elements whose linear dimensions are greater than twice the dimensions of the 16-atom groups having discrete frequencies of vibration. Thus, in the evaluation of the thermal energy of the crystal, we are concerned almost exclusively with vibrations localised in extremely small elements of volume in the crystal. We shall not be seriously in error in assuming such oscillations to be uncorrelated in phase as between different elements of volume and hence permitting of being quantised independently of each other.

Summary

The determination of the normal modes of atomic vibration in the earlier parts of the memoir also enables us to identify and enumerate the oscillators of which the quantised energies of vibration constitute the thermal energy of the crystal. Besides the oscillators with the nine discrete frequencies, there are others which give rise to a residual spectrum of vibrations with lower frequencies. The distribution of frequencies in that spectrum is determined and its contribution to the thermal energy is evaluated.