

The vibration spectra of crystals—Part V. Lithium and sodium fluorides

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Received November 27, 1947

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1. Introduction

Lithium and sodium fluorides are cubic crystals, their structure being of the NaCl type. The evaluation of their eigenfrequencies and the explanation of their spectroscopic behaviour are of particular interest for two reasons. Firstly, the low atomic weights of both the metal and the halogen and the strong interactions between the atoms in these fluorides result in their vibration spectra appearing at shorter wavelengths than with all the other alkali halides. Secondly, as the result of the disparity in atomic weights of metal and halogen in lithium fluoride, the modes in which the fluorine atoms alone oscillate have much lower frequencies than those in which the lithium atoms-alone or both lithium and fluorine atoms together oscillate. The atomic weights of sodium and fluorine do not differ so widely, and hence there is a closer approximation to each other of the various eigenfrequencies in the case of sodium fluoride. The spectroscopic behaviour of the two fluorides differs notably as the result of these circumstances.

2. Evaluation of the eigenfrequencies

As in the cases of NaCl and MgO, the nine eigenfrequencies can be calculated from the simplified theoretical formula containing only two force-constants, one

Table 1. Eigenfrequencies of lithium fluoride
($P = 1.02 \times 10^5$ dynes/cm, $T = -0.015 \times 10^5$ dynes/cm, m_H is the mass of the hydrogen atom.)

Designation	Description of mode	Degeneracy	$4\pi^2 c^2 m_H \nu^2$	Infra-red wavelength
ν_1	Normal oscillation of the cubic planes with <i>Li</i> and <i>F</i> atoms in same phase	3	$0.197P - 0.34T$	16.9μ
ν_2	Tangential oscillation of the cubic planes with <i>Li</i> and <i>F</i> atoms in opposite phases	6	$0.197P + 0.62T$	17.5μ
ν_3	Oscillation of <i>Li</i> and <i>F</i> lattices in opposite phase	3	$0.197P \pm 1.58T$	18.2μ
ν_4	Normal oscillation of <i>Li</i> atoms in octahedral planes with <i>F</i> atoms at rest	4	$0.144P - 1.15T$	19.0μ
ν_5	Tangential oscillation of <i>Li</i> atoms in octahedral planes with <i>F</i> atoms at rest	8	$0.144P + 0.58T$	20.7μ
ν_6	Normal oscillation of <i>F</i> atoms in octahedral phase with <i>Li</i> atoms at rest	4	$0.0527P - 0.42T$	31.4μ
ν_7	Tangential oscillation of <i>F</i> atoms in octahedral planes with <i>Li</i> atoms at rest	8	$0.0527P + 0.21T$	34.2μ
ν_8	Normal oscillation of cubic planes with <i>Li</i> and <i>F</i> atoms in opposite phase	3	$-1.23T$	56μ
ν_9	Tangential oscillation of cubic planes with <i>Li</i> and <i>F</i> atoms in same phase	6	$-0.62T$	80μ

Table 2. Eigenfrequencies of sodium fluoride
 ($P = 6.82 \times 10^4$ dynes/cm, $T = -0.10 \times 10^4$ dynes/cm, m_H is the mass of the hydrogen atom.)

Designation	Description of mode	Degeneracy	$4\pi^2 c^2 m_H \nu^2$	Infra-red wavelength
ν_1	Normal oscillation of cubic planes with Na and F atoms in same phase	3	$0.0961P - 0.01T$	30.0μ
ν_2	Tangential oscillation of cubic planes with Na and F atoms in opposite phases	6	$0.0961P + 0.38T$	30.9μ
ν_3	Oscillation of Na and F lattices in opposite phase	3	$0.0961P + 0.77T$	31.9μ
ν_4	Normal oscillation of F atoms in octahedral planes with Na atoms at rest	4	$0.0526P - 0.42T$	38.3μ
ν_5	Tangential oscillation of F atoms in octahedral planes with Na atoms at rest	8	$0.0526P + 0.21T$	41.8μ
ν_6	Normal oscillation of Na atoms in octahedral planes with F atoms at rest	4	$0.0435P - 0.35T$	42.2μ
ν_7	Tangential oscillation of Na atoms in octahedral planes with F atoms at rest	8	$0.0435P + 0.17T$	45.9μ
ν_8	Normal oscillation of cubic planes with Na and F atoms in opposite phases	3	$-0.76T$	87μ
ν_9	Tangential oscillation of cubic planes with Na and F atoms in same phase	6	$-0.38T$	125μ

of which is much larger than the other. The large constant P is practically fixed by the highest of the nine eigenfrequencies, while the small constant T completely determines the two lower frequencies and notably influences also the intermediate ones. P can be found at once, while T is so chosen as to fit the spectroscopic facts best over the whole range of observation. Table 1 shows the evaluation for the case of lithium fluoride and table 2 for the case of sodium fluoride, the values of P and T being in each case shown at the head of the table.

3. Absorption and reflection by lithium fluoride

Reinkober (1926) made some observations on the reflection and absorption of radiations in the near infra-red by lithium fluoride in the form of plates obtained by compressing the powder under high pressure. Later, Barnes (1932) studied the absorption curves in the remote infra-red by very thin films of the substance. The absorption, reflection and dispersion by single crystals have been investigated over a wide range of wavelengths by Korth (1932) and by Hohls (1937). As the result of these various studies, we have a picture of the spectroscopic behaviour of lithium fluoride which can be interpreted in the light of the theoretical results.

Table 1 shows that 16.9μ is the shortest wavelength in the first-order spectrum. 8.5μ and 5.6μ would therefore be the shortest wavelengths respectively in the second-order and third-order spectra of overtones and summations of the fundamental frequencies. We should accordingly expect a large increase in the absorption coefficient in passing from 5.6μ to 8.5μ and a further very large increase in passing from 8.5μ to 16.9μ . The absorption measurements made by Hohls for various wavelengths and thicknesses fully support these indications of the theory. Between 16μ and 35μ is a region of intense opacity as is to be expected. Hohls found a very weak but measurable transmission at 39μ and a notably larger transmission at 41μ . The measurements likewise show that a steep rise in the reflecting power starts at about 14μ and that a maximum of 78% is reached at 17μ . The reflection coefficient then diminishes a little and shows a minimum of 72% at 20μ . Beyond this wavelength it increases again and reaches a maximum value of 92% at 28μ . It then diminishes rapidly to 60% at 37μ and to 38% at 40μ , beyond which the fall is more gradual. The measurements of absorption in very thin films made by Barnes likewise show that the strongest absorption is in the region of wavelengths between 30μ and 35μ , the peak appearing at 32.6μ .

The facts recited above are readily understood on the basis that the first seven of the nine fundamentals listed in table 1 are rendered strongly active by reason of their coupling with the so-called "active" mode ν_3 , with the result that the whole range of wavelengths between 16.9μ and 34.2μ is one of intense opacity. The sixth and seventh fundamentals ν_6 and ν_7 represent the oscillations of the fluorine atoms against each other, the lithium atoms remaining at rest. Whereas the first reflection maximum between 15μ and 20μ is evidently due to the first five fundamentals which approximate to each other in frequency and form a group by

themselves, the second reflection maximum between $20\ \mu$ and $40\ \mu$ is evidently due to ν_6 and ν_7 , as also to various overtones and summations of the fundamental frequencies falling within this wavelength range. It is evident from the appearance of this second maximum of reflection, as well as from the fact that the strongest absorption by thin films is at $32.6\ \mu$ approximately midway between ν_6 and ν_7 , that these two fundamentals are strongly active and indeed more so than any of the fundamentals of higher frequency. This is a remarkable but not altogether surprising result, since in the case of MgO we found that the oscillations of the oxygen atoms against each other give the maximum of infra-red absorption. The explanation of the effect is presumably the same as in the case of MgO.

4. Absorption and reflection by sodium fluoride

The observations by Korth (*loc. cit.*) and by Hohls (*loc. cit.*) with crystal plates and of the absorption in thin films by Barnes (*loc. cit.*) give us the necessary data for the case of sodium fluoride. The clue to their understanding is likewise furnished by the activity of the eigenvibrations listed in table 2. In the present case, owing to the nearness of the atomic weights of sodium and fluorine, the four eigenfrequencies ν_4 , ν_5 , ν_6 and ν_7 form a group with their wavelengths $38.3\ \mu$, $41.8\ \mu$, $42.2\ \mu$ and $45.9\ \mu$ fairly close to each other. Their octaves likewise form a close group, the wavelengths being $19.2\ \mu$, $20.9\ \mu$, $21.1\ \mu$ and $23\ \mu$. The absorption by thin films is a maximum at $40.6\ \mu$, approximately midway between ν_4 and ν_5 which represent the oscillations of the fluorine atoms with the sodium atoms at rest. In this respect, the behaviour of sodium fluoride is analogous to that of lithium fluoride. On the other hand, there is only one reflection maximum instead of two as in lithium fluoride within the range of wavelengths covered by the first-order spectrum. This maximum of 90% is located at $35\ \mu$ and is evidently the resultant effect of all the seven active fundamentals. The increase in reflecting noticed for wavelengths greater than $20\ \mu$ with a maximum of 48% at about $23\ \mu$ in the second-order spectrum is evidently due to the group of octaves lying in the vicinity. The increase in the absorption coefficient between $19\ \mu$ and $24\ \mu$ observed by Hohls is likewise due to the same cause. No such effects are noticed with lithium fluoride, since in the latter case, $2\nu_7$ lies within the first-order spectrum, while $2\nu_6$, $2\nu_5$ and $2\nu_4$ are widely separated from each other in the second-order spectrum. Hohls has however observed a minor peak in absorption at about $12.9\ \mu$ which may be ascribed to several summationals falling in that region.

5. Summary

The eigenfrequencies of lithium and sodium fluorides have been theoretically evaluated and their observed spectroscopic behaviour is found to be in accord

with the results. The greater disparity in the atomic weights of metal and halogen in the case of lithium fluoride than in sodium fluoride leads to some interesting differences in behaviour between the two substances. In both cases, however, the frequency of maximum absorption does *not* correspond with the oscillation of the metal and halogen atoms against each other, but agrees with that of the oscillations in which only the fluorine atoms move, the metal atoms remaining at rest.

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