CHAPTER VI

Scattering of light in crystals

Introduction

61. The well-known influence of temperature ("Debye-effect") on the intensity of X-ray reflection as illustrated, for instance, in the experiments of Sir W H Bragg* on rock salt indicates that the atoms in the space lattice forming a crystal are not absolutely fixed but oscillate to some extent about a mean position; the magnitude of this effect differs widely for different crystals depending on the value of the "characteristic temperature" for the substance. Larmor† has suggested that this thermal movement of the atoms in the crystal should have an important consequence, namely that when a pencil of ordinary light traverses a transparent crystal, a certain portion of the incident energy should appear as scattered light. Such an effect, if observable, would furnish us with direct visual evidence of the reality of thermal oscillations in solids. No theoretical calculation of the magnitude of the expected effect has however appeared so far. Prof. R J Strutt‡ (now Lord Rayleigh) who experimented on the subject of the scattering of light in solids found that the track of a beam of light passing through a block of transparent quartz could be detected by photography and estimated that clear quartz scatters light 8 times as strongly as dust-free air. The effect was however ascribed by him to inclusions which he assumed were present in the quartz and not to the crystal itself. It occurred to the present author that observations with crystals such as rock-salt which show a marked Debye-effect would be of interest and that such crystals may be expected to show a strong scattering of ordinary light capable of direct visual observation. This expectation is shown to be justified by experiment, and it is found that even in the case of quartz in which owing to its high characteristic temperature the effect is weaker, direct visual observation of the scattering is possible.

Theory

62. A theoretical discussion shows that the observed effects are of the expected order of magnitude and are thus really due to the thermal agitation of the atoms in the crystal and not to the presence of inclusions in the crystal. The principles on which we must proceed become clear when we consider the hypothetical case of a crystal in which the atoms occupy fixed positions on a space-lattice, thermal movements being assumed to be non-existent. The size of a cell in the lattice being small compared with the wavelength of the incident light, the crystal may for practical purposes be regarded as a continuous homogeneous medium of *uniform optical density* and can accordingly scatter no light. As thermal movement disturbs the uniformity of the medium and introduces local fluctuations of optical density, the medium is no longer homogeneous but shows irregular variations of refractive index, which though small, nevertheless in the aggregate, result in an appreciable scattering of the light traversing the medium. The intensity of this scattering can be calculated if the average magnitude of fluctuation of optical density is known.

63. It has already been pointed out in the chapters on scattering in gases and liquids that precisely the same considerations result in the Einstein–Smoluchowski formula for the scattering power, namely,

$$\frac{\pi^2}{18}\frac{RT\beta}{N_1\lambda^4}(\mu^2 - 1)^2(\mu^2 + 2)^2$$

where β is the compressibility, μ the refractive index of the substance, λ is the wavelength of incident light and R, T, N_1 are the constants of the kinetic theory.

64. The success of Debye's theory and explaining the influence of temperature on X-ray reflection by crystals suggests that the Einstein–Smoluchowski theory (which is based equally with Debye's theory on the principles of statistical mechanics) should enable the scattering power of crystalline solids for ordinary light to be determined. An important reservation is however necessary owing to the known failure of the law of equipartition of energy in the case of substances with a high characteristic temperature such as diamond. The formula for the scattering power deduced on the assumption that the translatory kinetic energy of the individual atoms in the space-lattice is the same as that of the freely moving molecules in gases and liquids would obviously give us a result much in *excess* of the actual values.

65. The scattering power being directly proportional to the thermal energy, it is clear that in order to obtain the correct result, we should diminish the value given by the formula in the ratio which the actual heat-content of the solid at the temperature of observation bears to the heat-content determined on the principle of equipartition of energy. A calculation made on this basis and from the known compressibilities and refractive indices gives a scattering power for quartz about

Visual observations of scattering in crystals

66. In view of the fact that the scattering of light in dust-free air is easily visible, it is clear that the observation of the scattering of much greater magnitude in crystals indicated by the theory should be a simple matter provided the conditions necessary for success are attended to. Sunlight is evidently the best source of light to use in carrying out the experiment. A beam of it being admitted into a darkened room through an aperture and then focussed by a lens, the crystal is placed at the narrowest point of the cone of rays. In examining valuable material, it is a good plan to use a filter to cut out heat rays to avoid possible damage to the crystal. It is not at all necessary to use a large block of crystal. In fact quite a modest-sized piece of good quality will do, but it is of the highest importance that all the faces of the crystal should be scrupulously clean and highly polished so that they do not scatter light. The most suitable shape for the block is a cube or a rectangular parallelopiped held with one pair of faces quite square to the incident beam of light, the track of the cone of light inside the crystal being observed through another pair of faces. A natural cleavage block of transparent rock-salt thus seems very suitable for the observations. If a crystal, say of quartz, is of irregular shape or has oblique faces, a good plan of getting rid of stray light is to immerse the block in a square glass trough containing *clean* distilled water. A dark background should be provided against which the track of the light passing through the crystal should be viewed. Working in this way the scattering of light in clear colourless quartz is very readily observed visually. The Tyndall cone is quite uniform and of a beautiful blue colour closely matching that of the track of a concentrated beam of sunlight in saturated ether vapour and of about a third of its intensity so far as can be judged visually. The latter furnishes a convenient standard of intensity, and the observed result is thus of the order expected on theoretical grounds. Accurate measurements by a photographic method are at present being made in the author's laboratory by Prof. Lalji Srivastava.

67. By a similar method, light-scattering in rock-salt and in block ice can be very readily observed, the track being of a blue colour. In Iceland spar, the track is of a reddish tinge due apparently to a feeble fluorescence. This may be quenched by a suitable filter.

Polarisation of the scattered light

68. In making observations on the polarisation of the light scattered in crystals, account has to be taken of the doubly-refractive or optically active property of the material. In the case of quartz, the difficulty may be avoided by sending the beam of light in a direction transverse to the optic axis, and observing in a

this method, it is found that the light scattered transversely in quartz is not completely polarised, the track being quite clearly visible through a nicol. The cases of other crystals have not yet been thoroughly examined.

69. There is a noteworthy feature in which the light-scattering in crystals arising from the thermal movements of the atoms stands on a somewhat different footing from the case of light-scattering in liquids or gases. It has already been remarked in dealing with fluid media that the transversely-scattered light consists in part of *common* or *unpolarised* light even when the primary beam itself is completely polarised to begin with, and that this effect arises from the arbitrariness of the orientation of the molecules in such media. In crystals on the other hand, according to the current ideas, the positions and orientations of the atoms are more or less definitely fixed, subject only to small oscillations about the mean positions. If this be the case, we should expect that if the primary beam in the crystal is itself polarised, the transversely scattered light should also be polarised, though not necessarily in the same way as in the case of spherically symmetrical atoms. Observations have been made by the writer to test this point. In order more readily to detect the residual intensity of the track of the beam in the crystal, the method of "flicker" was used. The track was caused to vibrate slowly up and down in the crystal so that its existence or non-existence could be detected. It was found that the track of the beam could almost completely be quenched by observation through a nicol when the primary beam was itself polarised. But if the incident light was unpolarised, it always remained quite clearly visible in any position of the observing nicol. The matter however remains to be further tested by photographic methods.

Possible influence of temperature

70. As in the case of the Debye-effect, we should expect the light-scattering power of the crystal to be enhanced by rise of temperature. Some preliminary observations made with rock-salt seem to indicate that there is such an effect. The technique of experimentation on light-scattering with crystals placed in enclosures capable of being heated up or lowered in temperature without damage to the surface of the crystal requires however to be further developed.