

Raman and Infra-red Spectra of Rock-salt

RASSETTI¹ succeeded in recording a Raman spectrum with rock-salt, using the 2537 Å. radiations of the mercury arc as exciter. But as neither his preliminary report nor his subsequent paper with Fermi² gives quantitative details of the spectrum, it appeared desirable to investigate the subject afresh. In seeking to record the Raman effect with rock-salt, the presence of a disturbing effect became evident, namely, a luminescence exhibited by the crystal attended by the development of a fugitive coloration under the action of the ultra-violet rays. As the Raman spectrum is itself feeble, it is partially masked or even completely overpowered by the continuous spectrum of the luminescence. Ultimately, however, a specimen of rock-salt was found which was non-luminescent. Using this specimen, and with a fine slit which made prolonged exposures necessary, a spectrogram was obtained in which much more detail could be seen than in the picture reproduced with Rasetti and Fermi's paper. As is evident from its microphotometric record here reproduced, the spectrum consists of a series of Raman lines distinctly resolved from each other. The frequency shifts from the parent radiation of the more prominent of them are 135, 184, 235, 278*, 314* and 350* cm.⁻¹, while there are feebler lines with frequency shifts 202 and 258 cm.⁻¹. Further, there are indications that the three lines marked with an asterisk possess imperfectly resolved components.

It is worthy of note that Barnes and Czerny³, investigating the infra-red absorption spectrum of sputtered films of rock-salt, found, besides the principal absorption peak at 163 cm.⁻¹, other absorption peaks at 190 and 245 cm.⁻¹, the latter being the more prominent. The experimental method of locating these peaks is sufficiently uncertain to justify our identifying their positions, at least tentatively, with that respectively of the two lines with frequency shifts 184 and 235 cm.⁻¹ which appear very prominently in the Raman spectrum. There is no Raman line with a shift 163 cm.⁻¹ corresponding to the frequency of the principal infra-red absorption; but this is not surprising as symmetry considerations⁴ indicate that it should not appear in light-scattering. We may, however, tentatively identify the Raman line with frequency shift 314 or one of its components as the octave of the principal infra-red active vibration frequency.

The appearance with rock-salt of numerous clearly defined and well-resolved Raman lines, other than the octave of the so-called 'fundamental frequency' of the lattice, is clearly a matter of great theoretical interest. The theories of light-scattering in crystals^{5,6} which are based on Born's postulate of the cyclic lattice, lead to the result that only the infra-red vibrations the length of the phase-waves of which satisfies the well-known Bragg formula in relation to that of the light waves, can give an observable effect. This is equivalent to the statement that only the so-called 'fundamental vibration frequencies of the crystal lattice' can appear in the Raman effect, and that all others are excluded. Pursuing the same train of thought to its logical conclusion, it can readily be shown that if the second-order terms in the variations of optical polarizability and/or the anharmonicity of the vibrations are considered, octaves and/or combinations of the 'fundamental vibration frequencies' may appear, and no others.

In the attempt to escape the contradiction with the experimental facts which is manifest, we may give up the assumption (inherent in the postulate of the cyclic lattice) that the infra-red vibrations have coherent phase-relations over extended volumes in the crystal, and limit the region of assumed coherence of phase to volume elements the dimensions of which are large compared with an individual lattice cell, but are smaller than the wavelength of light. Even this change in the basis of the theoretical approach, however, does not resolve the difficulty. For, on the new basis, the entire continuous spectrum of the crystal as deduced from the Born dynamics should manifest itself as

a second-order Raman spectrum of octaves and combinations. What we actually get, however, is something very different, namely, a set of discrete lines.

The contradiction between the experimental facts as observed with rock-salt and the consequences of the Born crystal dynamics would, therefore, seem to be inescapable.

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¹ Rasetti, F., *Nature*, **127**, 626 (1931).

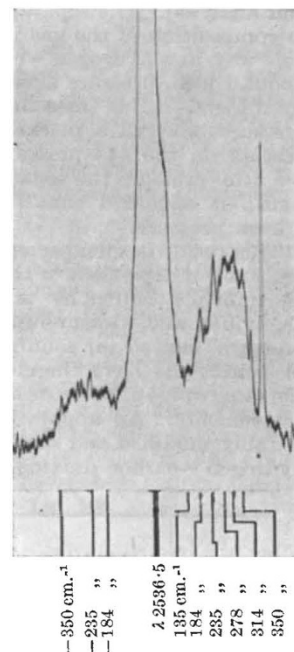
² Fermi, E., and Rasetti, F., *Z. Phys.*, **71**, 689 (1931).

³ Barnes, R. B., and Czerny, M., *Z. Phys.*, **72**, 441 (1931).

⁴ Schaefer, C., *Z. Phys.*, **54**, 153 (1929).

⁵ Mandelstam, Landsberg and Leontowitsch, *Z. Phys.*, **60**, 334 (1930).

⁶ Tamm, I., *Z. Phys.*, **60**, 345 (1930).



Microphotometric record of the Raman spectrum of rock-salt

Effect of Pressure on Thermal Diffusion in Gases

BECAUSE of the present interest in the industrial application of thermal diffusion to the separation of gases, it is perhaps desirable to report some work concerned with the effect of pressure on the thermal diffusion process.

Schmahl and Schewe published measurements¹ of the separation produced by thermal diffusion in mixtures of hydrogen and hydrogen sulphide, and of hydrogen and carbon dioxide. The gas mixture was contained in two cylindrical bulbs, 2 cm. in diameter and 21 cm. and 7 cm. in length respectively. The bulbs were connected by a 5 mm. bore tube, 12 cm. long, which included a stopcock. While the larger vessel was heated in a furnace, the other was maintained at 20° C., and when equilibrium was attained the contents of the two bulbs were separately removed