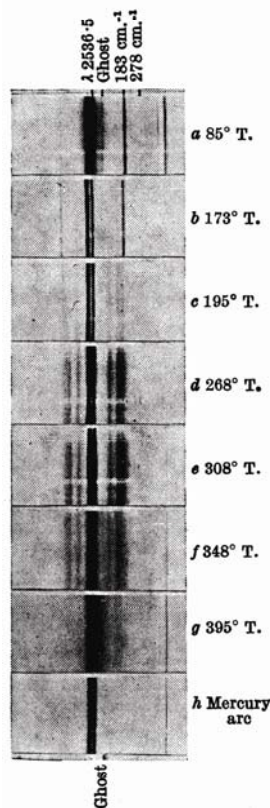


### Vibration Spectra of the Alkali Halides

As is well known, ammonium chloride crystallizes in the cubic system, its structure being of the rock-salt type above 450° T. and of the caesium chloride type below that temperature.



Menzies and Mills<sup>1</sup> found that at liquid air temperatures it shows in its Raman spectrum a strong line with a frequency shift of 183 cm.<sup>-1</sup>. This observation is significant, since the frequency shift corresponds to the *Reststrahlen* frequency of the crystal<sup>2</sup> and hence indicates that the oscillation of the NH<sub>4</sub> groups against the Cl ions is Raman-active. The crystal powder technique employed by Menzies and Mills is, however, not well suited for the study of Raman spectra in the region of such small frequency shifts. Accordingly, a fresh investigation has been made with a well-grown single crystal and the  $\lambda$  2536.5 excitation and the same technique as in my recent investigations with various other crystals. To enable the entire sequence of changes to be observed, spectra were recorded with the crystal held at a series of seven temperatures down to that of liquid air.

The series of spectra reproduced, while confirming Menzies and Mills' results for the liquid air temperature, reveals numerous other interesting facts. The spectrum becomes diffuse and faint when the crystal is heated up above room temperature. *Per contra*, when the crystal is cooled down, the spectrum brightens and also sharpens remarkably, exhibiting even above the so-called  $\lambda$ -point transition (243° T.), a group of three fairly well-defined Raman shifts of 92, 141 and 170 cm.<sup>-1</sup> respectively, with indications of two fainter ones at 107 and 195 cm.<sup>-1</sup>. These persist far below the  $\lambda$ -point transition, becoming at the same time quite sharp and showing a progressive shift in their position with falling temperature. A remarkable change in their relative intensities also occurs at the same time. At liquid air temperatures, a new line with a frequency shift of 278 cm.<sup>-1</sup> unmistakably makes its appearance. This is quite sharp but faint.

There can be little doubt that the features seen in the spectra reproduced arise from oscillations of the lattice in which the NH<sub>4</sub> groups may be considered to move as single units and that, with the exception of the 278 cm.<sup>-1</sup> line, they represent the first-order vibration frequencies of the lattice. The observed discrete character of the spectrum and the sharpening of the lines with falling temperature are both in accord with the fundamental ideas regarding the vibration spectra of crystal lattices put forward by Sir C. V. Raman<sup>3</sup> and are, therefore, experimental evidence of his theory. That the vibration frequencies in this case are Raman-active in the first order, instead of being inactive as in the metallic halides, is evidently a consequence of the NH<sub>4</sub> group possessing only tetrahedral symmetry as compared with the octahedral symmetry of the metallic ions.

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<sup>1</sup> Menzies and Mills, *Proc. Roy. Soc., A*, **148**, 407 (1935).

<sup>2</sup> Rubens and von Wartenberg, *Ber. Deut. Chem. Ges.*, **69** (1914).

<sup>3</sup> Raman, *Proc. Ind. Acad. Sci., A*, **18**, 237 (1943).