Raman Spectrum of Strontium Fluoride (SrF_2)

The fluorides of calcium, strontium and barium form an isomorphous series of compounds belonging to the space group O_h^5 with molecular unit of three atoms in each unit cell. The lattice dynamics of calcium fluoride has been worked out by GANESAN and SRINIVASAN[1]) and the validity of the Lyddane-Sachs-Teller (LST) relation for this crystal has been established. Recently the infrared absorption of the fluorides of calcium, strontium and barium has been studied in detail by KAISER et al.[2]) and the frequencies corresponding to the transverse optical mode appearing in infrared absorption of these crystals have been accurately estimated. Because of the high symmetry, only the mode corresponding to the oscillation of the two fluorine lattices against each other, metal lattice remaining at rest, is expected to appear in the first order Raman spectrum. The observed frequencies of Raman spectra in CaF_2 [3]) and BaF_2 [4]) have the values 321.5 cm^{-1} and 244 cm^{-1} respectively. The Raman spectrum of SrF_2 has not been investigated so far.

A clear piece of artificially grown SrF_2 of size $10 \times 4 \times 4$ mm was made available to the authors by Dr. R. MELLER. The specimen was found to be transparent to the ultraviolet. Its Raman spectrum was therefore recorded using a Hilger medium Quartz spectrograph and the λ 2536.5 Å resonance radiation of mercury as exciter (Fig. 1). As is to be expected the spectrum exhibits only a single Raman shift of 285 cm^{-1}, however, this Raman line was found to be asymmetric with the presence of a wing on the higher frequency side. A similar observation has already been made in the case of BaF_2 by NARAYANAN and NEELAKANTAN[5]) who also noticed an asymmetric broadening of the Raman line when the temperature was raised. With intense exposures the spectrum of SrF_2 exhibited not only a strong line at 285 cm^{-1}, but also a weak continuous spectrum extending from the exciting line to a few hundred wave numbers.

The infrared active mode in these crystals splits up into two according to the LST formula and the values reported[2]) are given in the Table.

The study of the fluorescence and absorption spectra of CaF_2, SrF_2 and BaF_2 doped with Sm^{2+} ions has shown the existence of lines on the long wave-length side of the main fluorescent band, due to forced electric dipole transitions and

Table. *Infrared and Raman frequencies and force constant data for CaF_2, SrF_2 and BaF_2*

	ν_f*)	ν_c*)	R	$\gamma(X-Y)$	α_1**)	α_3**)	Z^2
CaF_2	257	463	321.5	2.36 Å	$1.68 \cdot 10^4$	$1.22 \cdot 10^4$	0.605
SrF_2	217	374	285.0	2.50 Å	$1.525 \cdot 10^4$	$0.745 \cdot 10^4$	0.603
BaF_2	184	326	244.0	2.68 Å	$1.28 \cdot 10^4$	$0.40 \cdot 10^4$	0.65

*) $\nu_f = \nu_1$ (TO) frequency found in infrared absorption, $\nu_c = \nu_1$ (LO) value calculated using the LST relation. Values in cm^{-1} taken from [2]). R = Raman frequency in cm^{-1}. $\gamma(X-Y)$ nearest neighbour distance.

**) Notation for force constants and expressions α_1, α_2, Z used are the same as given in [1]). Lattice constant for SrF_2 $2\gamma_0 = 5.78$ Å.

that the separation of one component in each crystal corresponds to the Reststrahlen frequency of the particular host lattice[6]). In the case of SrF_2 the frequency separations observed are 216 and 282 cm^{-1}. The former obviously corresponds to the infrared frequency ν_1 (TO) of 217 cm^{-1} observed in absorption [2]). No infrared absorption was found at 282 cm^{-1}. But the present study shows that it corresponds to the frequency of the Raman active mode and lends support to the interpretation of the fluorescence spectrum of SrF_2 Sm^{2+} given earlier[6]).

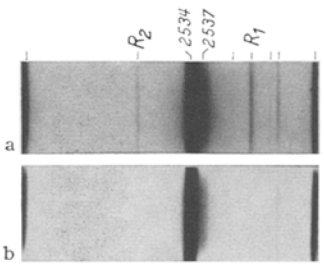

Fig. 1. a Raman spectrum of SrF_2. b Comparison mercury spectrum. R_2 and R_1 Raman lines (285 resp. − 285 cm^{-1})

A calculation of the force constants was made using the expressions by GANESAN and SRINIVASAN[1]) and the values compared with those obtained for CaF_2 and BaF_2. α_1 is the force constant for the nearest neighbour interaction, α_3 that for the second neighbour interaction and Z is the effective charge. Comparing the values of the force constants given in the Table, it is seen that the second neighbour interaction (α_3) decreases more rapidly than the nearest neighbour interaction (α_1) as one goes from calcium to barium. The calculated force constant α_1 for CaF_2, SrF_2 and BaF_2 seems to be inversely proportional to the square of the nearest neighbour distance, showing thereby that the nearest neighbour interaction is mainly of the Coulomb type. The next neighbour interaction force constant does not follow any such proportionality.

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