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FAR-INFRARED SPECTRUM AND PHASE TRANSITION OF $CsSrCl_3$

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Temperature dependence of the far-infrared spectrum of $CsSrCl_3$ has been measured. At high temperature the spectrum has three absorption bands, which is characteristic to the cubic perovskite-type structure. Lowering the temperature, one new band appears at 153 cm^{-1}. Other spectral change is not significant. The new band is interpreted as an i.r. active component of a f_{2u} mode for the high temperature phase which undergoes a factor group splitting in a phase transition to the lower symmetry phase.

It has been reported by an X-ray powder diffraction measurement that the structure of $CsSrCl_3$ at room temperature is the perovskite-type with a tetragonal distortion and the space group is $C_{4v}{}^{1}$-P4mm with one chemical unit in a unit cell.1) A reversible heat effect occurs at 125 to 130°C.1) Although there has been no experimental evidence, the structure of the high temperature phase has been considered to be the cubic perovskite-type, which is characteristic to the perovskite-type crystals.

We have measured the far-infrared spectrum of $CsSrCl_3$ at various temperatures. A spectral measurement has been made for the powder sample dispersed in the Nujol using a Hitachi 070 far-infrared interferometer. As shown in Fig. 1, three absorption bands are observed above 180°C. With lowering the temperature, a new absorption appears at 153 cm^{-1} and increases its intensity. The spectral change with temperature is reversible.

The optically active lattice vibrations of the cubic perovskite structure are $3f_{1u} + f_{2u}$, of which the $3f_{1u}$ modes are infrared active. The spectrum above 180°C may be explained by this cubic structure. According to the $C_{4v}{}^{1}$ structure for the low temperature phase, each of the f_{1u} modes splits in two i.r. active species, a_1

and e, and a f_{2u} mode splits in an i.r. active e mode and an inactive b_1 mode. Therefore, the new band which appears in the lower temperature phase can be assigned to the e mode of the C_{4v}^1 structure which arises from a f_{2u} mode in the cubic phase.

If $CsSrCl_3$ is isomorphous to $CsPbCl_3$ as suggested by Pozdnyakova et al,2) the feature of the low temperature spectrum might be more or less alike those for the structures of phase II (D_{4h}^5-P4/mbm, Z=2, $\Gamma = a_{1g} + a_{2g} + b_{1g} + b_{2g} + e_g + 2a_{1u} + 3a_{2u} + 2b_{2u} + 7e_u$), phase III ($D_{2h}^{17}$- Cmcm, Z=8, $\Gamma = 7a_g + 7b_{1g} + 6b_{2g} + 4b_{3g} + 6a_u + 9b_{1u} + 8b_{2u} + 10b_{3u}$), and phase IV ($C_{2h}^2$-$P2_1$/m, Z=4, $\Gamma = 14a_g + 10b_g + 15a_u + 18b_u$) of $CsPbCl_3$.3-5) Then we may expect much more complicated spectrum. Actually we have observed only one new band in the low temperature spectra. Therefore the interpretation based on the structure isomorphous to $CsPbCl_3$ may not be acceptable. Apart from the appearance of a new band, the spectral change is not appreciable as a whole. Therefore a structural distortion may not be significant.

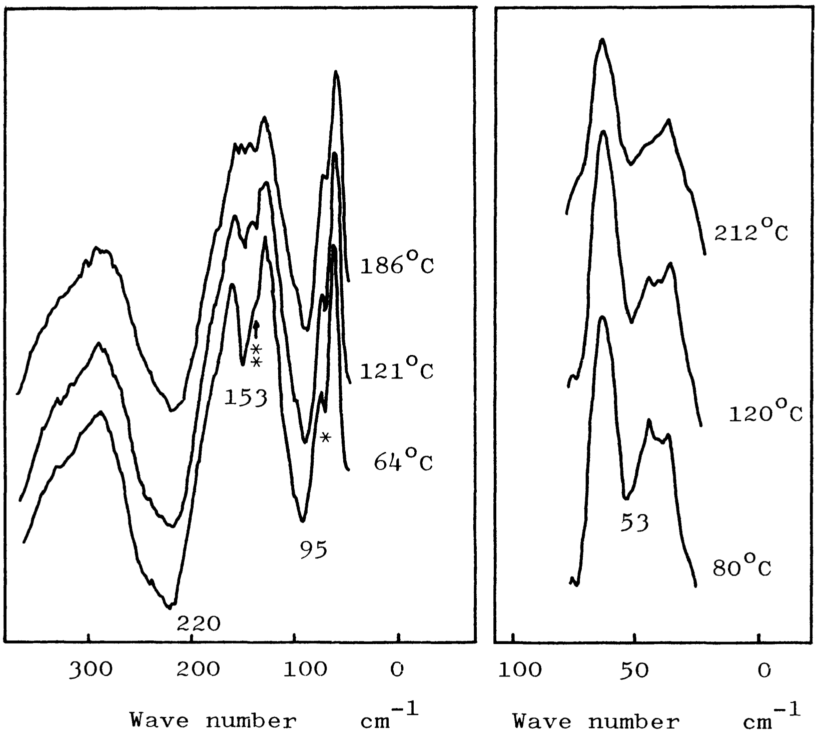

Fig. 1. Far infrared spectrum of $CsSrCl_3$ at various temperatures. * and ⁑ are the absorptions of polyethylene and quartz, respectively.

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