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RAMAN SCATTERING FROM PHONONS IN DISORDERED $CsMg_{1-x}Co_xCl_3$

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Abstract.- Five zone-centre phonons have been measured at low temperatures and for a range of concentrations in $CsMg_{1-x}Co_xCl_3$. Three E_{2g} modes and the A_{1g} mode all exhibit the expected one-mode behaviour. A new theory is required to explain the unusual concentration dependence of the E_{1g} phonon intensity, lineshape and polarisation.

1. Introduction.- The lattice dynamics of AMX_3 compounds have been widely studied and many possess the $CsMgCl_3$ structure (see figure 1) of space group D^4_{6h} with two formula units in the primitive cell. A factor group analysis predicts $A_{1g}+E_{1g}+3E_{2g}$ Raman active modes. The A_{1g} and E_{1g} modes comprise chlorine ion motions, perpendicular and parallel to the c (Z) axis respectively, while the E_{2g} modes involve halogen and cesium ion displacements in the hexagonal (X,Y) plane. We have studied the mixed crystal $CsMg_{1-x}Co_xCl_3$ to clarify assignments of phonons in $CsMgCl_3$[1,2] and $CsCoCl_3$[1,3] and thereby assist the interpretation of the highly structured magnon spectrum of $CsCoCl_3$.[3]

2. Experiment and Results.- Large single crystals of $CsMg_{1-x}Co_xCl_3$ were grown with concentrations in the ranges $0 \leqslant x < 0.2$ and $0.6 < x \leqslant 1$. Raman spectra were excited with 100 mW of 476.5 nm argon laser light in the 90° scattering geometry X(••)Y, analysed with a double monochromator (2 cm^{-1} resolution), and recorded under computer control. Polarised Raman spectra for pure $CsMgCl_3$ recorded at 5 K allowed unambiguous assignments of phonon lines at 55.0, 127.5, 132.0, 189.0 and 255.0 cm^{-1} to symmetry species E_{2g}, E_{1g}, E_{2g}, E_{2g} and A_{1g}, respectively. The A_{1g} mode showed no anomalous (YX) intensity in contrast to that found earlier.[1] Figure 2 presents part of the results obtained for the mixed crystals. The scattering from E_{2g} and A_{1g} phonons follows D_{6h} selection rules for all concentrations and only the A_{1g} and E_{2g} (132 cm^{-1}) modes show appreciable frequency shifts with increasing x. All of these phonons exhibit one-mode behaviour as predicted by theory.[4]

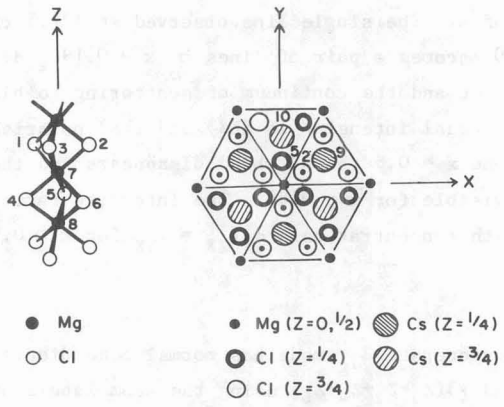

Fig. 1: Details of the $CsMgCl_3$ crystal structure.

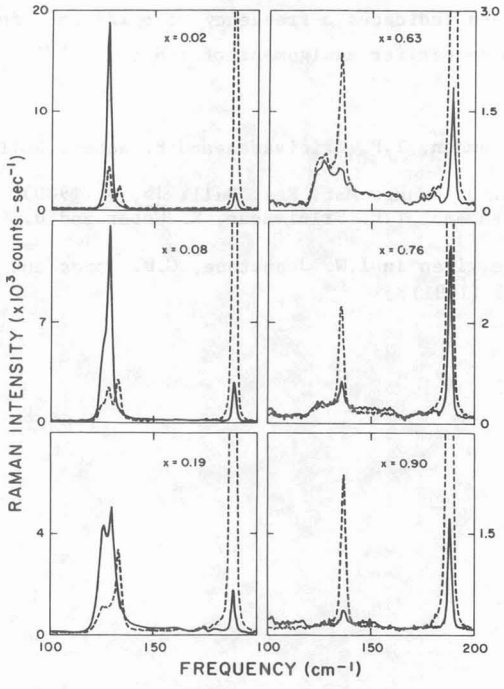

Fig. 2: Concentration dependence of the X(ZX)Y (——) and X(YX)Y (---) Raman spectra for phonons in $CsMg_{1-x}Co_xCl_3$ at 5 K.

Figure 2 shows the dramatic changes in band shape and intensity for the E_{1g} phonon as a function of x. The single line observed at 127.5 cm^{-1} in (ZX) polarisation for x = 0 becomes a pair of lines by x = 0.19. By x = 0.63 this fine structure has smeared out and the continuum of scattering to higher frequency is now more prominent and has equal intensity in (ZX) and (YX) polarisations. As x is further increased beyond x = 0.8 the E_{1g} band disappears and the continuum becomes weaker, being barely visible for x = 0.88. The intensity ratio I_{ZX}/I_{YX} for the E_{1g} phonon also changes with concentration and $I_{ZX} \approx I_{YX}$ for x > 0.63, contrary to D_{6h} selection rules.

3. Discussion.- The degenerate E_{1g} mode has normal mode displacements of the form[4] $Z_1+Z_2-Z_4-Z_6-2Z_3+2Z_5$ and $\sqrt{3}(Z_1-Z_2+Z_4-Z_6)$ using the atom labels of figure 1. Therefore the Raman cross-section for this mode should be relatively insensitive to substitution of the divalent metal ion, and the other Raman active modes behave sensibly in this respect. Thus although the E_{1g} mode frequency is concentration independent the lineshape, polaristion and intensity behave anomalously. Extrapolation of our data indicates a frequency of ~ 127 cm^{-1} for the E_{1g} mode in $CsCoCl_3$, as opposed to an earlier assignment of 118 cm^{-1}.[1,3,4]

References
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4. Further details are given in I.W. Johnstone, G.D. Jones and D.J. Lockwood, Solid St. Commun. 39, 395 (1981).