Chapter V

CONCLUSION

Infrared and Raman spectra of pure potassium chromate and potassium sulphate crystals were reported in this study. These two methods gave complimentary but nonidentical information. Vibrational multiplet structure in crystals originated from site group effects and correlation field (or factor group) effects, so the phenomenon was discussed in terms of these two effects.

The site symmetry of both the cations and anions is C_s in both potassium chromate and potassium sulphate, so the spectral data were discussed in term of C_s site group symmetry. Furthermore, it was demonstrated that all the anions had local C_3 axis lying in a crystallographic mirror plane approximately parallel to the z-axis. The hidden symmetry of a crystal structure C_{3v}, not evident in the space group D_{2h}^{16}(Pnma), played a key role in the vibrational spectra of crystals.

All internal modes predicted by the site group and factor group approximations could be identified. However, it was important to note that in several cases the two modes of different symmetry had the same frequency,i.e. accidental degeneracies. The number of observed infrared and Raman frequencies

was less than the number of internal modes allowed by the selection rules because of the accidental degeneracies and the low resolution.

The study of potassium chromate/potassium sulphate mixed crystals was to investigate separately the site group and factor group effects. The infrared and Raman spectra of the molecular ions in the mixed crystals differed from the spectra of those in the pure crystals. The frequencies were shifted and the degeneracies were lifted . The major interaction between molecular ions was due to long range dipolar coupling and the dipolar coupling between like molecular ions was much greater than between unlike molecular ions, then the addition of impurities would decrease the dipolar coupling between the host ions. The magnitude of the frequency shift was different for modes of different symmetry as the nature of the dipolar coupling differed for modes of different symmetry. In general, the most strongly active vibrations showed the largest shifts.

In the high dilution limit of mixed crystals, the guest ions were matrix isolated and therefore vibrationally uncoupled, i.e. chromate ions (guest ions) isolated in a host of potassium sulphate matrices and sulphate ions (guest ions) isolated in a host of potassium chromate matrices. The splittings of the guest ion modes resulted only from the site group effects. or became a direct measure of the anion site symmetry. It was found that, in the triply degenerate antisymmetric stretching ν_3 band

of the guest ion, the individual components were much sharper and the splitting of the ν_3 components were significantly reduced. Because of the band narrowing, maxima were observed for the ν_3 components in both of potassium chromate and potassium sulphate which showed a triplet structure in their infrared spectra.

The effect of isolation was to :

1. Reduce the bandwidth of individual components.
2. Reduce the spacing.
3. Alter the relative intensities of the components.

The spectral data from a pure crystal to dilution limit of mixed crystals showed that the magnitude of the total splittings were decreased by 10 $cm.^{-1}$. The total splittings were the sum of site group and factor group splittings, therefore, the factor group splitting was 10 $cm.^{-1}$. In the analysis of the vibrational spectra of crystals it was usually found that the site group effects were more important than factor group effects. The result in this study suggested that such conclusions should be treated with caution because the site group effects might contain the factor group effects.

The X-ray powder diffraction patterns (diffractograms) of the mixed crystals were compared with those of pure compounds and mixtures. The diffractograms of the mixed crystals were intermediate between the diffractograms of the two pure compounds while the diffractograms of the mixtures were superposition of them,

this difference indicated the existence of the mixed crystals. The unit cell dimensions of the mixed crystals and pure compounds were calculated from the X-ray powder diffraction data. The unit cell dimensions of the mixed crystals were intermediate between those of the separate components. The unit cell parameters were found to vary linearly with the composition of the mixed crystals. The spectral data showed that the frequency was shifted to higher when the lattice parameter of the matrix was decreased, this tendency was expected if the long-range electrostatic forces were the cause of the frequency shift. So it was concluded that the increase in frequency of the ν_1, ν_3 modes resulted from the decrease in unit cell dimensions.