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Tetrahedral Cobalt(II) Ions in an MX_2 Layer Lattice

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Many first row transition metal dihalides crystallize as layer lattices of the cadmium chloride or cadmium iodide type [1]. These structures consist of layers of halide ions close packed in either a cubic ($CdCl_2$) of hexagonal (CdI_2) manner with the metal ions filling every second layer of octahedral holes. Every second successive pair of chloride layers is in intimate contact with no interspersed metal ions. This rather covalent structure allows quite an extensive range of solid solutions of transition metal ions to be formed in host lattices of cadmium or magnesium halides.

Until now, the transition metal ion has substituted into the larger octahedral holes in the lattice. Examples of this type include cobalt(II) ions doped into cadmium chloride [2] and bromide [3] and into magnesium chloride in low concentrations [4]. Using a technique for the *in situ* production of transition metal ions in molten magnesium chloride [5], we have been able to grow single crystals of magnesium chloride doped with about 20% cobalt(II) ions in which some of the cobalt ions are present in the tetrahedral sites.

Figure 1 shows the 10 K electronic spectrum of a doped magnesium chloride crystal grown from the melt by the Bridgeman technique. The bands above 17,000 cm^{-1} are typical of octahedral cobalt(II) and are due to the $^4A_{2g} \rightarrow {}^4T_{1g}$ (^4P) and $^4A_{2g} \rightarrow {}^2T_{1g}$ (^2P) transitions. The bands below 17,000 cm^{-1} correspond to a new tetrahedral cobalt site and refer mainly to the $^4T_{1g} \rightarrow {}^4T_{1g}$ (^4P) transition and its associate vibronic structure. The tetrahedral peaks increase in intensity and the octahedral peaks decrease in intensity as the temperature is lowered. This behaviour is as expected for a partially allowed and vibronically allowed transition respectively. The oscillator strength of the visible spectrum of tetrahedral cobalt(II) is greater than that of octahedral cobalt(II) and the spectrum indicates that between 5 and 10% of the cobalt ions are in tetrahedral sites. In a second crystal prepared separately, the ratio of octahedral to tetrahedral occupancy varied by a few percent but the relative intensities of the bands for each species considered separately remained the same. Using magnesium bromide as a host, a lower occupancy of the tetrahedral sites was observed (Fig. 1).

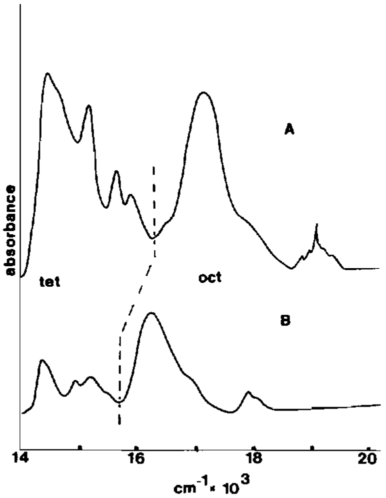
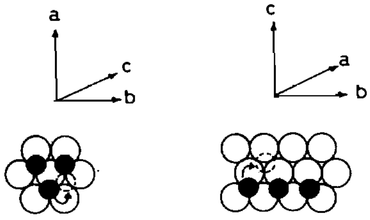


Fig. 1. 10 K spectra of magnesium chloride (A) and magnesium bromide (B) doped with about 20% cobalt(II) ions. Spectra were taken along the *c* axis.

This tetrahedral cobalt ion is the first clear example of a cation in a layer lattice of this type which is not isomorphously substituted for the host cation and it is unusual in that the tetrahedral site is sufficiently small to require a relaxation of the lattice structure to accommodate the cobalt. There are two possible replacement sites, namely the tetrahedral site in the same layer as the octahedral metal ions (A) and the tetrahedral site between the layers (B).



The site **B** would seem to create the least additional energy and this might help to explain how those lattices can incorporate some ions into octahedral holes even when the ion is larger than the hole itself [4]. Such occupancy of the vacant sites in the layer between the metal ion layers has important implications because an unusual impurity site with an associated vacancy in the filled metal ion layer is created and because it will affect the complex magnetic ordering present in halides heavily doped with cobalt ions. This latter process has been extensively studied in pure transition metal dihalides and both ferromagnetic and antiferromagnetic coupling of the ions have been identified. For example in cobalt chloride the ferromagnetic ordering is along

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the layers and the antiferromagnetic ordering is across the layers. The presence of the interstitial cobalt ions would be expected to modify this magnetic structure.

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