AN EPR AND ESEEM STUDY OF Fe(CN)\(_6^{3-}\) IN KCl SINGLE CRYSTALS


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An EPR and ESEEM study was made at \(~15K\) on the ferricyanide complex in KCl lattice for a further investigation of the large compensation mechanism of trivalent impurity ions in alkali-metal halides [1,2]. A large number of Fe(CN)\(_6^{3-}\) centres were found through EPR spectra. Due to the complexity of the spectra, detailed analysis only was possible for three centres. They are all at the low spin state, i.e., \(S=1/2\). The dominant centre, which makes more than 60% of the total occupancy, has an orthorhombic symmetry. The three principal g-values, \(g_z=0.4\), \(g_x=2.079\) and \(g_y=3.056\), are found when B [100], [011], and [011], respectively. A second centre is very similar to the dominant centre, having the same symmetry, but possessing a different set of g-values. The third centre has monoclinic symmetry with the symmetry determined principal axis along \(\langle110\rangle\). These centres are due to the Fe(CN)\(_6^{3-}\) complex with different configurations of the local charge compensating cation vacancies. Models are proposed for the three identified centres and a comparison is made between Fe(CN)\(_6^{3-}\) in KCl and the Cr(CN)\(_6^{3-}\) complex in both KCl and NaCl. The relaxation times, both \(T_1\) and \(T_2\) were measured as a function of orientation and temperature by the Electron Spin Echo (ESE) technique. The Electron Spin Echo Envelope Modulation (ESEEM) was used to study the interaction with the nitrogen nuclei of the CN ligands.