The Spectrum of Ti^{2+} Ions isolated in a Sodium Chloride Crystal

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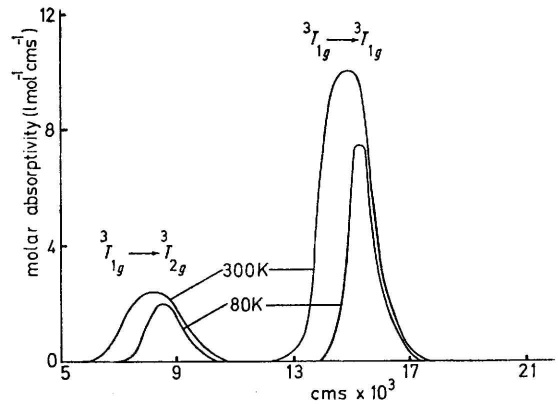
Summary Spectra of Ti^{2+} ions isolated in a sodium chloride crystal are in agreement with the predictions of ligand field theory.

With the exception of spectra in melt systems,[1] the ligand field spectrum of Ti^{2+} is not known, since in compounds of Ti^{II}, the valence state is purely formal and the spectra, where these have been measured, bear no relation to a normal spectrum for two unpaired *d* electrons.

This communication describes the isolation of Ti^{2+} ions in a sodium chloride crystal and spectral measurements on the crystal which are in good agreement with the predictions of ligand field theory.

Sodium chloride was chosen as a host matrix because the Na^+ ion is about the same size as the Ti^{2+} ion and sodium



chloride melts in the temperature range in which Ti^{II} is predicted thermodynamically to be the most stable valence state for chloride systems. It seemed likely that once the Ti^{2+} ions were trapped in the crystal, the valence state would be stabilized as, for example, are divalent rare earth ions.[2] The Ti^{2+} ion was created by reacting cadmium chloride and titanium metal in a sodium chloride melt at 950 °C. The cadmium metal produced sublimed out of the melt. The solid was transferred to a silica tube, sealed under vacuum and grown as a crystal by the Bridgeman technique. The resultant crystals were analysed for titanium and on average the atomic ratio Ti/Na was 0·5%. Care was taken throughout to exclude moisture and oxygen from the system and i.r. transmission spectra of the crystals showed no evidence of hydroxide or other impurity.

The spectra obtained are as expected for a transition metal ion with two unpaired electrons in an octahedral environment. The two main absorption bands are $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$. Values of Dq and B derived from the 77K spectrum are 852 cm^{-1} and 572 cm^{-1} respectively.

The likely intensity mechanism is vibronic and the bands show a marked drop in intensity and a shift to higher energies of the peak position as the temperature is lowered. The total oscillator strength of the bands are consistent with this intensity mechanism.

Magnetic measurements were difficult to carry out due to the low concentration of paramagnetic ion but the results obtained were in reasonable agreement with two unpaired electrons in the system.

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[1] H. A. Oye and D. M. Gruen, *Inorg. Chem.*, 1963, **2**, 836.

[2] M. Wagner and W. E. Bron, *Phys. Rev. A.*, 1965, **139**, 223.