The Single Crystal Infrared Electronic Spectrum of Ni^{2+}/Cs_2ZnCl_4 and Ni^{2+}/Cs_2ZnBr_4

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Summary An electronic *d–d* transition within the $^3T_1(F)$ ground state of tetrahedral Ni^{2+} is reported for the first time.

There have been numerous studies of the electronic spectrum of tetrahedral Ni^{2+} in the range 4000—25,000 cm^{-1} but as yet no observation of any of the transitions within the $^3T_1(F)$ ground manifold. Such an observation is of interest since bands arising from within the ground state are not perturbed in first order by the tetrahedral field. Wiekliem,[1] in his study of the spectrum of tetrahedral Ni^{2+} systems, attempted to observe these transitions in the i.r. but was unsuccessful, presumably because his doping level of Ni^{2+} was too low.

In the far i.r. and i.r. energy regions, the broad and relatively weak electronic bands of tetrahedral nickel complexes are invariably obscured by the phonon spectrum. In this paper we report electronic bands in the i.r. region for Ni^{2+}/Cs_2ZnCl_4 and Ni^{2+}/Cs_2ZnBr_4 where the host lattice is transparent down to *ca.* 400 cm^{-1}.

Both crystals were grown from the melt by the Bridgeman technique from a mixture of anhydrous NiX_2 and Cs_2ZnX_4 where X = Cl or Br. The atomic weight ratio of Ni^{2+} to Zn^{2+} is *ca.* 1—20. Sections suitable for spectroscopic measurements† were cut and polished and mounted in a variable temperature cryostat.

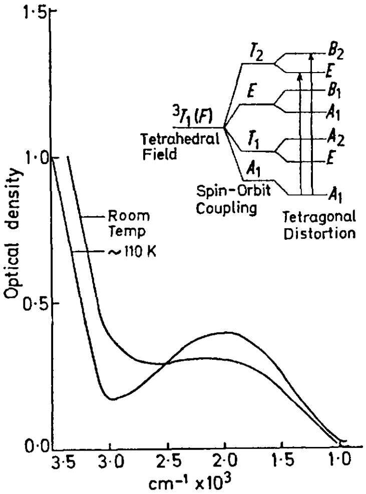

Figure. *The* $A_1 \rightarrow (E,B_2)$ *transition in* Ni^{2+}/Cs_2ZnCl_4.

Both Cs_2ZnCl_4[2] and Cs_2ZnBr_4[3] belong to the space group D_{2h}^{16} with four molecules per unit cell. The symmetry of the ZnX_4^{2-} unit is C_s but to a reasonable approximation can be taken as D_{2d} and, for the purposes of a crystal field calculation and selection rules, we have used the latter

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† Spectra were recorded on a Perkin-Elmer 457 grating i.r. spectrophotometer.

point group. From a comparison of crystal structure data the bromide is known to be more distorted than the chloride.

The electronic spectrum of Ni^{2+}/Cs_2ZnCl_4 at room temperature and *ca.* 110 K is shown in the Figure. Similar spectra were obtained for Ni^{2+}/Cs_2ZnBr_4 where the band maximum lay at about the same energy position as the chloride.

Only transitions to E or B_2 states will be allowed in D_{2d} symmetry and on the basis of a crystal field calculation[4] we have assigned our spectra as $A_1 \rightarrow E,B_2(T_2)$, the two electronic components being unresolved. The band intensity is dependent on the concentration of Ni^{2+} ions and we discovered that for crystals with different doping levels, the ratio of the oscillator strengths of this band to the $^3T_1(F) \rightarrow {}^3T_2(F)$ band is approximately constant with a ratio of 1:11 respectively. We therefore assign the new band to a single centre transition. We have also measured the host lattice under similar instrument and sample conditions and obtain a flat base line both at room temperature and 110 K.

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