d–d Spectra of Titanium(II) and Vanadium(II) Ions doped into a Sodium Chloride Host Lattice

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The preparation of sodium chloride crystals doped with titanium(II) and vanadium(II) ions is described and the homogeneity of the samples considered. Temperature-dependent electronic spectra of the ligand-field bands are reported and the results fitted to a coth $(\theta/2T)$ expression. At low temperature, vibronic progressions of 9—11 units are observed on some bands. The information which may be obtained from the spectra regarding the geometry of the site and the nature of the vibronic coupling is discussed.

ELECTRONIC spectra arising from *d–d* transitions on titanium(II) and vanadium(II) ions have been recorded on a number of occasions but, in general, there have been fewer studies of these ions than of many first-row transition-metal ions. Because the spectra of pure compounds of $\mathrm{Ti^{II}}$ and $\mathrm{V^{II}}$ are made more complex by interactions between metal ions[1] and because many compounds containing them are sensitive to moisture and oxygen, studies of these species doped into relatively inert host matrices are of some interest. Recently, work has been concerned mainly with these ions in uni- or bi-axial host environments.[1-3]

Titanium(II) and vanadium(II) ions are of about the same size as sodium ions and both may be doped into sodium chloride crystals.[3,4] A major problem with all ion-doped systems, and one which is not always considered, is to ensure that the ions are present as isolated entities and not doped into the host in a non-homogeneous way. We attempted to resolve this in the present study. The spectra of the impurity sites are reported and the information they yield regarding both the nature of the impurity site and the little studied problem of the coupling of electronic wavefunctions of impurity ions with lattice modes is discussed.

EXPERIMENTAL

Sodium chloride (B.D.H.) was dried in an oven at 200 °C for 24 h, transferred to a silica tube, and melted *in vacuo*. After 30 min the tube was cooled, filled with nitrogen, capped, and transferred to a dry-box. The NaCl was removed, crushed, and added to a second clean dry silica tube together with weighed amounts of cadmium chloride and titanium or vanadium metal powder. The second tube was capped, returned to the vacuum line, evacuated, and sealed.

The sealed tube was suspended in a furnace at 900 °C for 2—3 h to allow the titanium or vanadium metal to react and for all the cadmium metal to distil out of the melt. The furnace was constructed so that there was a sharp temperature gradient in the lower half. The crystal was grown by lowering the tube slowly, over a period of *ca.* 48 h, through the gradient.

Crystals grown in this manner had titanium and vanadium levels of *ca.* 1% of the total cation concentration. Samples for spectroscopic study and analysis were cleaved from the crystals and, if necessary, polished with Diamyx paste. The spectra were recorded on a Beckman Acta IVM u.v.-visible near-i.r. spectrophotometer. The cryostat was an Air Products Displex closed-cycle refrigerator with a base temperature of 7—8 K. It was equipped with a temperature controller. Samples were mounted on the copper cold finger with Air Products Crycon grease. A Thor digital temperature meter, connected to a gold–iron thermocouple with the cold tip mounted on the cold finger beside the sample, was used for temperature measurement. Analysis of selected samples to enable oscillator strengths to be calculated was by atomic absorption spectrometry using flame atomisation. Peak areas were measured with a planimeter.

RESULTS AND DISCUSSION

Preparation of the Samples.—Temperatures of 900—950 °C at the hottest point on the tube were required to ensure that the charge was completely molten. Since titanium dichloride tends to dissociate to titanium and chlorine at these temperatures it was found more convenient to prepare the ion *in situ*. In this case reaction[4,5] (1) was selected since it was found that the cadmium

$$\mathrm{CdCl_2 + Ti \longrightarrow TiCl_2 + Cd} \qquad (1)$$

metal could be distilled out of the melt more or less completely. Excess of titanium metal was used to reduce the possibility of cadmium ions being incorporated into the crystal. Any tendency for the titanium ions formed to be reduced to the metal would have been decreased by the overpressure of chlorine generated in the sealed tube. Titanium mirrors were formed on the edges of the tube, but provided the charge was kept molten, until the crystal-growing stage was initiated, clear, green, well formed sodium chloride crystals containing titanium ions were obtained. Crystals containing vanadium(II) ions can be prepared equally well either by the dissolution of vanadium dichloride in NaCl or by a similar method to that described for titanium, using vanadium instead of titanium metal. The latter method was employed for the production of the crystals used in this study since it eliminated the necessity of preparing pure $\mathrm{VCl_2}$ as a starting material. There was no evidence of the formation of appreciable amounts of vanadium metal and the cadmium metal was clearly visible condensed on the walls of the tube above the melt.

Sample Homogeneity.—Many studies of the spectra of ions in crystals grown from melts assume that the ion is in solid solution or at least is in an environment that approximates to it. However, the composition range in which solid solution is found in crystals formed from mixed melts is very variable and often not very large. Should the composition chosen for crystal growth lie outside the solid solution range, it is likely that the excess of dopant may be ' zone refined ' out of the system by the crystal-growing procedure. However, it is also possible that nucleites either of the dopant or a reaction product of the dopant and the host melt may be included in the growing crystal. In this study attempts were made to prepare cobalt(II)- and chromium(II)-doped sodium chloride crystals by the dissolution of cobalt and chromium halides in molten NaCl and subsequent crystal growth by the methods described above. It appeared initially that both cobalt and chromium ions were successfully doped into the lattice to produce blue and colourless (slightly milky) crystals respectively. The spectra were as expected from ligand-field predictions. However, on microscopic examination, these crystals were seen to be inhomogeneous, consisting of sodium chloride crystals with well dispersed small nucleites containing the transition-metal ions.

The cobalt and chromium samples were not studied further and it may well be that successful ion-doped specimens of sufficient concentration for spectroscopic study can be obtained by altering the experimental parameters. However, these attempts raised questions concerning the nature of the vanadium and titanium crystals which had appeared quite homogeneous under microscopic examination.

Three observations appear to confirm that the titanium and vanadium ions can be regarded as isolated impurities in the lattice. First, when the crystals were grown, they were of up to 5 cm in length. Apart from impurities at the top and foot of the tube and, in the case of titanium, on the walls, the crystals were clear, clean, and evenly coloured with no evidence of striations or ion-concentration gradients. Secondly, to try and detect small nucleites, a laser beam was directed in turn through crystals doped with each of the four metal ions. There was considerable scattering from the cobalt- and chromium-doped samples whereas with titanium- and vanadium-doped samples the beam could only be observed at crystal imperfections and surfaces, indicating that any nucleites were too small to scatter the Raman light to any appreciable extent. Finally, pairing or clustering of transition-metal ions often increases the intensity of spin-forbidden relative to spin-allowed bands. For example, in a study of the visible and near-i.r. spectra of vanadium compounds, the spin-forbidden bands in VCl_2, $KVCl_3$, and V^{2+} doped into cadmium chloride [1,4] all showed spin-forbidden levels which were easily detected when the largest band in the ligand-field spectrum had an absorbance of about one. In the present study, the spin-forbidden bands are so weak that only one, very close to a spin-allowed peak and possibly gaining intensity from it, has been observed. It therefore seems reasonable to assume solid solution for the vanadium and titanium ions.

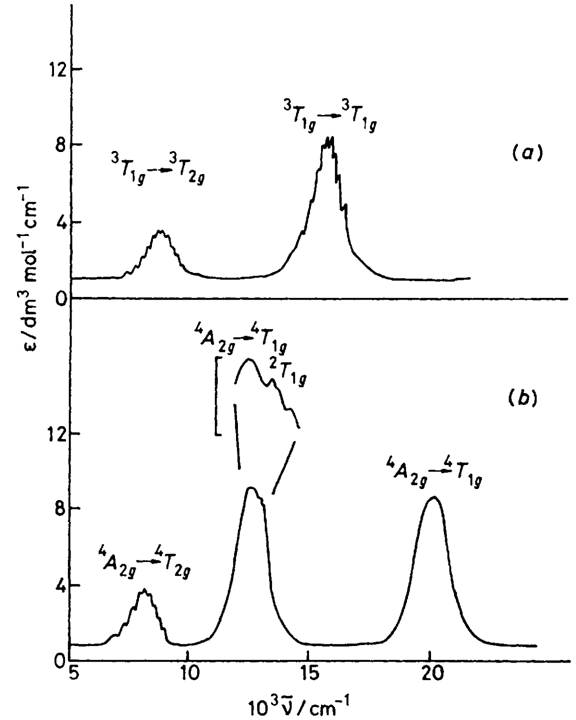

FIGURE 1 Ligand-field spectra at 10 K of (a) titanium(II) and (b) vanadium(II) ions doped into a sodium chloride host

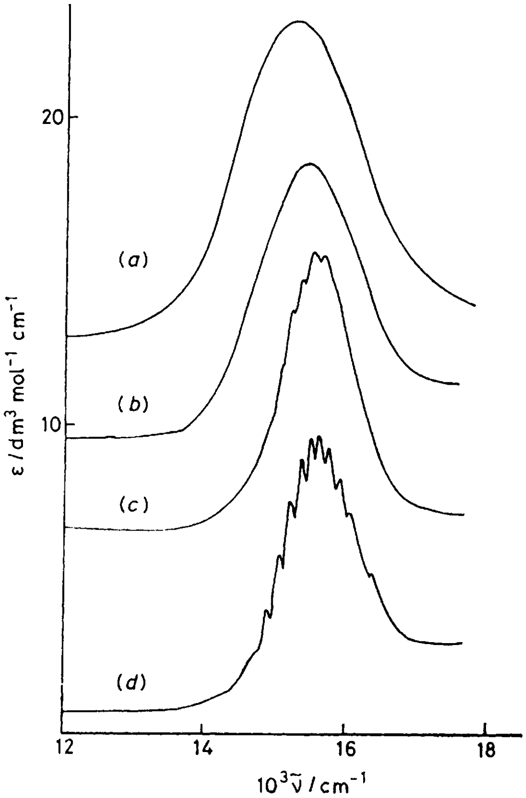

FIGURE 2 Temperature dependence of the spectra of the $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$ transition of titanium(II) ions doped into a sodium chloride host at (a) 293, (b) 200, (c) 100, and (d) 10 K

Ligand-field Assignments.—The spectra at 10 K are consistent with an octahedral site for both ions (Figure 1). The assignment of the three bands in vanadium to

$^4A_{1g}\rightarrow{}^4T_{2g}$,$^4A_{2g}\rightarrow{}^4T_{1g}(F)$ and $^4A_{3g}\rightarrow{}^4T_{1g}(P)$ and of the two in titanium to the $^3T_{1g}(F)\rightarrow{}^3T_{2g}$ and $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$ transitions is quite straightforward. The $^3T_{1g}(F)\rightarrow{}^3A_{2g}$ transition of titanium is usually weak and is not observed clearly here. Dq values of 850 and 780 cm^{-1} and B values of 615 and 570 cm^{-1} for the titanium and vanadium systems respectively are reasonable. There is no evidence in these spectra of band splittings of the type noted for Ti in $CdCl_2$ and interpreted in terms of the Jahn–Teller effect,[2] nor is there evidence of band splittings due to a low-symmetry field component such as would seem to appear in the spectrum of V^{2+} doped into the orthorhombic host lattice $KCdCl_3$.[3]

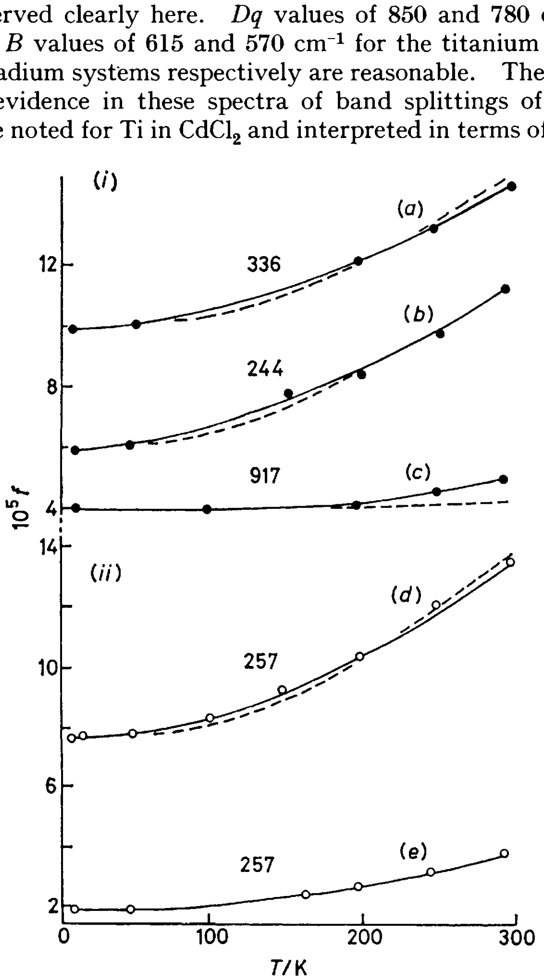

FIGURE 3 Temperature dependence of the oscillator strengths of the ligand-field bands of (*i*) vanadium(II) and (*ii*) titanium(II) ions in a sodium chloride host. Broken lines indicate the results predicted when the expression $f = f_0 \coth(\theta/2T)$ is fitted to the results at 200 K. The values on the curves are the vibrational frequencies obtained from the coth expression (in cm^{-1}). For the $^3T_{1g}\rightarrow{}^3T_{2g}$ transition of titanium, the difference between theoretical and experimental expressions is small. Transitions: (*a*) $^3A_{2g}\rightarrow{}^4T_{1g}(F)$, (*b*) $^4A_{2g}\rightarrow{}^4T_{1g}(P)$, (*c*) $^4A_{2g}\rightarrow{}^4T_{2g}$, (*d*) $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$, and (*e*) $^3T_{1g}(F)\rightarrow{}^3T_{2g}(F)$

Temperature Dependence.—An example of the temperature dependence of the spectra is shown for the $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$ band of Ti^{II} (Figure 2). In all the bands there is a shift in the maximum to higher wavelengths and a drop in oscillator strength as the temperature is decreased (Figure 3). However, these effects are much less marked with the $^4A_{2g}\rightarrow{}^4T_{2g}$ band of vanadium. A similar observation has been made for the $^3A_{2g}\rightarrow{}^3T_{2g}$ band of Ni^{II} in $KMgCl_3$.[6] Previous polarisation measurements had indicated a large contribution to the intensity from a magnetic dipole-allowed component of this transition.[7] Possibly a similar argument may apply in this case.

The exact form of the temperature dependence of the oscillator strengths of the ligand-field bands of octahedrally co-ordinated transition-metal ions is still a matter of some doubt. However, the expression $f = f_0$-coth$(\theta/2T)$ has been tested for octahedral nickel ions [6] and, having regard to the lower and shorter temperature ranges used here, would seem a reasonable one to compare with the spectra.

Since the value of f_0 can be estimated fairly exactly from the spectra at 10 K, the expression was fitted to the experimental value of f at 200 K to give values of θ. The $^4A_{2g}\rightarrow{}^4T_{2g}$ band in vanadium-doped NaCl has too low a temperature dependence to be reasonably tested by this expression and further the θ value required corresponds to an allowed vibrational frequency at 917 cm^{-1} which is too high to be reasonable. With this exception, the experimental oscillator strengths are in reasonable agreement with the calculated ones.

Other values of θ used give vibrational bands which vary from 244 to 336 cm^{-1}, and seem quite reasonable. The allowed vibrations are probably best regarded as asymmetric vibrational modes of the impurity centre but they lie in an energy region above the Restrahlen band frequency in which various combination modes of the sodium chloride host lattice can be observed in the i.r. spectrum. One of the postulates of the model from which the coth expression is derived is that the spectra arise from a single allowed vibration in each case.[6] It is interesting, therefore, that the titanium bands appear to require the same vibrational frequency and it is in the case of titanium and of the $^4A_{2g}\rightarrow{}^4T_{2g}$ band in vanadium already discussed that resolved fine structure is obtained.

Fine Structure.—The most notable feature is the development of a regular progression of 9—11 units in both titanium peaks and the $^4A_{2g}\rightarrow{}^4T_{2g}$ vanadium band (Figure 1). The regularity and degree of resolution obtained in each progression is similar and is illustrated for the $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$ band of titanium (Figure 2). The results are consistent with a vibronic coupling mechanism for an octahedrally co-ordinated ion.[8] The vibrational interval of the $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$ progression in the titanium-doped sample is 168 ± 3 cm^{-1} and in the vanadium-doped sample is 173 ± 3 cm^{-1}. Considering the difference in size and electronic structure of the ions, these results might well indicate progressions in the same symmetric mode arising from similarly shaped impurity centres. However, the $^3T_{1g}(F)\rightarrow{}^3T_{1g}(P)$ band in the titanium-doped sample has a progression interval of 112 ± 3 cm^{-1} which would seem to indicate coupling with another mode.

In the case of the $^3T_{1g}(F)\rightarrow{}^3T_{2g}(P)$ transition of titanium, very poorly resolved fine structure was observed on one of the peaks in the progression but a greater degree of resolution, such as might result from still lower sample temperatures, would be required to characterise such structure, which may be due to either spin–orbit coupling or a low-symmetry field component.

The reasons why two of the vanadium bands do not give resolved progressions at 10 K is not clear. Attempts were made to resolve structure on these bands, but it must be assumed that either the vibronic selection rules arising from the different symmetry states give rise to more complex overlapping progressions or that the natural linewidths are broader.

The three lines near the peak of the ${}^4A_{2g}\rightarrow{}^4T_{2g}(F)$ band of vanadium (Figure 1) are relatively sharp and irregularly spaced and tentatively assigned to the ${}^4A_{2g}\rightarrow{}^2T_g$ spin-forbidden band of vanadium.

The Geometry of the Impurity Site.—The spectroscopic evidence suggests that the transition-metal ions are in octahedral sites. There is no evidence of distortion of the band shapes although such evidence is found for environments only slightly distorted from octahedral,[1,3] and the temperature dependence of the spectra suggests that the site is centrosymmetric. A reasonable initial interpretation is to consider that the transition-metal ion is at the centre of an octahedral impurity site in the sodium chloride lattice, and that the spectra arise from a vibronic mechanism involving the localised modes of the impurity centre.

The vacancy required to compensate for the extra charge on the transition-metal ion appears not to influence the spectrum to any appreciable extent although an effect has been found in the sharper lines in rare-earth-doped crystals.[9] In the present case, at 850 °C with *ca.* 1% doping levels the vacancy need not always be closely associated with the metal ion and its subsequent position at room temperature will depend on the rate of annealing of the crystals during growth. However, at least a fraction of the metal ions would be expected to have a vacancy on the next-nearest-neighbour sodium-ion site and the lack of any very appreciable indication of the distortion would seem to reflect the relative rigidity of the sodium chloride lattice and the similar sizes of the transition-metal ions to that of sodium ions.

The different frequencies observed in the progressions in the spectra of the titanium(II)-doped sample highlight a little investigated area, namely the selection rules for vibronic processes which involve coupling with lattice or localised-impurity modes rather than internal vibrations of a molecular or complex ion. In this case, the indications are that a single, and possibly the same, allowed vibration is active in each case but the products of the symmetry species of the electronic states and the electric-dipole operator will be different, resulting in different vibronic states. The vibrational interval for the progression observed in the ${}^3T_{1g}(F)\rightarrow{}^3T_{2g}(F)$ transition lies in the gap between the optic and accoustic modes of NaCl and consequently is best assigned to a localised mode of the centre. The allowed vibration(s) and the other progression frequency lie at or above the Restrahlen band frequency (To at the Brillion zone centre) and may be due either to localised or lattice modes. The vibration of the impurity centre will be coupled to the lattice modes in any case and the symmetries of the lattice vibrations will vary depending on the position in the Brillion zone. Therefore, the spectra probably contain more information than that used concerning the nature of the impurity centre but a fuller explanation is best left until a better understanding, both experimental and theoretical, of the nature of vibronic coupling in this type of impurity centre has been developed.

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