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# Absorption Spectrum of $Cr^{3+}$ Doped in Ammonium Chloride Single Crystal

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*Results of optical absorption at 300° K and 80° K of $Cr^{3+}$ ion doped in $NH_4Cl$ are reported. The observed bands have been assigned transitions from the ground $^4A_{2g}$ (F) state to the excited $^4T_{2g}$ (F), $^2E_g$ (G), $^2T_{1g}$ (G) and $^4T_{1g}$ (F) states. From the nature and position of the bands a successful interpretation of all the observed bands could be made assuming tetragonal site symmetry for the $Cr^{3+}$ ion in the crystal. The crystal field parameters derived are $Dq = 1480\ cm^{-1}$, $Ds = -800\ cm^{-1}$, $Dt = -48\ cm^{-1}$, $B = 680\ cm^{-1}$* and $C = 3060\ cm^{-1}$.

*The value of $35\ cm^{-1}$, obtained for spin–orbit coupling parameter in the present work is found to be in very good agreement with the ESR value of $34\ cm^{-1}$.*

## Introduction

Parker[1] studied the electron spin resonance spectrum of $Cr^{3+}$ ion doped in ammonium chloride crystal and reported at 77° K, $g_x = 1.9795$, $g_y = 1.9798$, $g_z = 1.9859$, $E = 0.247$ GH$_z$ and $D = 3.189$ GH$_z$, where D and E are the zero field splitting parameters and g is the spectroscopic splitting factor. From the observed features, he suggested the possibility of a small rhombic distortion in the crystal. He also reported that the $Cr^{3+}$ ions are incorporated interstitially in the ammonium chloride lattice.

Since the optical absorption spectrum of $Cr^{3+}$ : $NH_4Cl$ has not been reported in literature so far, the authors took up the present investigation for the first time.

## Experimental

Single crystals of $Cr^{3+}$ doped in $NH_4Cl$ were kindly supplied by Dr. Pilbrow. The optical absorption spectrum was recorded from 9000 Å to 3000 Å on a Hilger medium quartz spectrograph, both at room and liquid air temperatures. The spectra were recorded in about 10 to 20 minutes on Kodak IN and Ilford R-40 plates. Using microphotometric profiles recorded on a Moll microphotometer, the wavelengths of the band maxima were measured against iron arc standard lines in a similar way as has been done by Pappalardo[2] and Lakshman *et al.*[3]

## Results and Analysis

The spectrum observed at room temperature showed three main bands around 20044, 17950, and 14810 cm$^{-1}$. When the crystal had been cooled to liquid air temperature, the intensity of all the bands improved considerably and three sharp line–like bands have been recorded at 15212, 15272, and 15392 cm$^{-1}$. The bands obtained at liquid air temperature are shown in Figure 1, and the microphotometric profile of these bands is shown in Figure 2. In addition, a band at 14394 cm$^{-1}$ has also been developed as a shoulder to the moderately intense band at 14810 cm$^{-1}$.

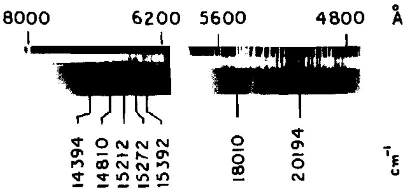

Figure 1. Medium quartz spectrogram of $Cr^{3+}$ in $NH_4Cl$ at 80° K.

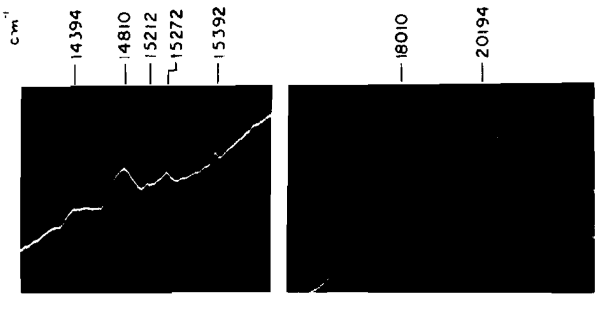

Figure 2. Microphotometric profiles for the absorption bands of $Cr^{3+}$ in $NH_4Cl$ at 80° K.

## Discussion

From the nature and observed features of the bands they have been attributed to the $Cr^{3+}$ ion. Assuming $O_h$ symmetry for the $Cr^{3+}$ ion in the complex, the ground state electronic configuration can be written as $^4A_{2g}(F)$. We therefore expect three spin allowed bands for this ion corresponding to $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$, $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(P)$ transitions. The two observed intense bands have therefore been attributed to the electronic transitions $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ respectively.

For $Cr^{3+}$ in $O_h$ symmetry, we expect sharp bands for the electronic states $^2E_g(G)$, $^2T_{1g}(G)$ and $^2T_{2g}(G)$ which arise from the same ground state electronic configuration of $(t_{2g})^3$. The energy of the $^2T_{2g}(G)$ would be considerably higher than that of $^2T_{1g}(G)$ or $^2E_g(G)$. Since the bands observed at 15212 $cm^{-1}$ and 15272 $cm^{-1}$ are quite sharp and close to one another, they both have been attributed to the same electronic transition $^4A_{2g}(F)\rightarrow{}^2E_g(G)$ while the sharp band at 15392 $cm^{-1}$ has been assigned to the transition $^4A_{2g}(F)\rightarrow{}^2T_{1g}(G)$.

From the observed band positions, the values of B and Dq determined from the Tanabe and Sugano diagram[4] for $d^3$ configuration are $B = 680\ cm^{-1}$ and $Dq = 1480\ cm^{-1}$.

Since in solid systems the $Cr^{3+}$ sites are seldom crystallographically $O_h$, we expect splitting of the bands due to lower symmetry fields such as tetragonal or trigonal. The observed weak bands at 14394 $cm^{-1}$ and 18010 $cm^{-1}$ which appear as components of 14810 $cm^{-1}$ and 20194 $cm^{-1}$ bands are an indication of the lowering of symmetry in the crystal.

Assuming that the transitions to $^2E_g(G)$ and $^2T_{1g}(G)$ borrow all their intensity from the first spin allowed transition $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ we obtain,

$$\frac{f(^4A_2\rightarrow{}^2E)}{f(^4A_2\rightarrow{}^2T_1)} = \frac{[^4T_2|V_{SO}|^2E]^2}{[^4T_2|V_{SO}|^2T_1]^2} \qquad (1)$$

where $f(^4A_2\rightarrow{}^2E)$ and $f(^4A_2\rightarrow{}^2T_1)$ are the oscillator strengths for the $^2E_g(G)$ and $^2T_{1g}(G)$ bands respectively and $(^4T_2|V_{SO}|^2E)$, $(^4T_2|V_{SO}|^2T_1)$ are the spin–orbit matrix elements. Since the squares of these spin–orbit matrix elements are each equal to $16\,\xi^2$ and $6\,\xi^2$ ($\xi$ is the spin–orbit coupling coefficient) respectively, we have

$$\frac{f(^4A_2\rightarrow{}^2E)}{f(^4A_2\rightarrow{}^2T_1)} = \frac{16\,\xi^2}{6\,\xi^2} = \frac{8}{3} = 2.7 \qquad (2)$$

It is interesting to note from the observed oscillator strengths given in Table I, that this theoretical ratio of 2.7 is in good agreement with the experimental ratio of 2.3.

From ESR studies on $Cr^{3+}$ in $NH_4Cl$ crystal, Parker observed a slight rhombic distortion in the crystal. We may therefore, without much error assume tetragonal distortion in the crystal in the interpretation of the observed bands, as has been done by Parker in the calculation of the Spin–orbit and crystal-field parameters.

Using the energy expressions given by Peruma Reddy[5] for $d^3$ configuration the tetragonal field parameters (Ds, Dt) derived are $Ds = -800\ cm^{-1}$, $Dt = -48\ cm^{-1}$.

The observed energies of the bands along with their designations in octahedral and tetragonal symmetries are presented in Table I.

Since the values of Ds and Dt are approximate as they are evaluated from the splitting of only two bands, no attempt has been made to calculate the energy levels using the quadrate energy matrices given by Peruma Reddy and compare them with the observed band positions.

The value of the spin–orbit splitting coefficient ($\lambda$) for $Cr^{3+}$ in ammonium chloride is evaluated from the $g_{\parallel}$ and $g_{\perp}$ parameters given by Parker (from ESR studies) and the band positions of $^4B_2$ ($^4T_2$) and $^4E$ ($^4T_2$) observed in the present work as follows:

$$g_{\parallel} = 2.0023 - \frac{8\lambda}{\Delta} \qquad (3)$$

and

$$g_{\perp} = 2.0023 - \frac{8\lambda}{\Delta'} \qquad (4)$$

where

$$g_{\parallel} = g_z,\ g_{\perp} = g_x = g_y$$

$$\Delta' = E(^4B_1) - E(^4E)$$

and

$$\Delta = E(^4B_1) - E(^4B_2).$$

TABLE I. Experimental Data and Analysis of the Absorption Spectrum of $Cr^{3+}$ Doped in $NH_4Cl$.

| Octahedral Transition from $^4A_{2g}(F)$ | Observed Energies at 300° K $cm^{-1}$ | Observed Energies at 80° K $cm^{-1}$ | Tetragonal Transition from $^4B_1$ | f Values at 300° K | f Values at 80° K |
|---|---|---|---|---|---|
| $^4T_{2g}(F)$ | 14810 | 14394 | $^4E$ | – | $1.3 \times 10^{-6}$ |
| | | 14810 | $^4B_2$ | $3.4 \times 10^{-5}$ | $3.8 \times 10^{-5}$ |
| $^2E_g(G)$ | – | 15212 | $^2A_2$ | | |
| | | 15272 | $^2B_1$ | – | $11.8 \times 10^{-7\,a}$ |
| $^2T_{1g}(G)$ | – | 15392 | $^2E$ | – | $5.2 \times 10^{-7}$ |
| $^4T_{1g}(F)$ | 17950 | 18010 | $^4E$ | $1.7 \times 10^{-4}$ | $1.21 \times 10^{-4}$ |
| | 20044 | 20194 | $^4A_2$ | $2.1 \times 10^{-4}$ | $1.38 \times 10^{-4}$ |

[a] Integrated intensity.

Using

$$\Delta = 14810\ \mathrm{cm}^{-1},\ \Delta' = 14394\ \mathrm{cm}^{-1}$$

$$g_{\parallel} = 1.9859 \text{ and } g_{\perp} = \frac{g_x + g_y}{2} = 1.9797$$

the values of $\lambda$ obtained from equations (3) and (4) are 30 $\mathrm{cm}^{-1}$ and 40 $\mathrm{cm}^{-1}$ respectively. The average value of $\lambda$ thus comes out to be 35 $\mathrm{cm}^{-1}$.

Using the following expression, which is valid for $Cr^{3+}$ ion (Pryce[6], Abragam and Pryce[7]):

$$\lambda = \frac{4\,D}{(2\,g_z - g_x - g_y)}$$

the value of $\lambda$ calculated with $D = 3.189$, $GH_z = 0.105\ \mathrm{cm}^{-1}$ (Parker) is 34 $\mathrm{cm}^{-1}$. It is interesting to find that this value is in good agreement with the value (35 $\mathrm{cm}^{-1}$) obtained in the present work.

The reduction factor $k = \dfrac{\lambda}{\lambda(\text{free ion})}$ calculated with the value of $\lambda = 35\ \mathrm{cm}^{-1}$ (present work) and $\lambda$(free ion) = 91 $\mathrm{cm}^{-1}$ (Moore[8]) is rather small (0.38). The value of k quoted by Owen and Thornley[9] for chrome alum is 0.6, while Sugano and Tanabe[10] reported a value of about 0.5 for $Cr^{3+}:Al_2O_3$. Parker is of the opinion that a more reasonable value of the reduction factor k (of the order of 0.6) could be obtained, if a higher order of accuracy in the measurement of the *g* parameter were available. However, Abragam and Bleany[11] point out that quite often we obtain a low value for $\lambda$ and this they think is due to the inadequacy in the theory.

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