

ON THE OPTICAL ABSORPTION SPECTRA OF $\text{Ni}^{2+} \cdot 6\text{H}_2\text{O}$ COMPLEX IN CRYSTALS

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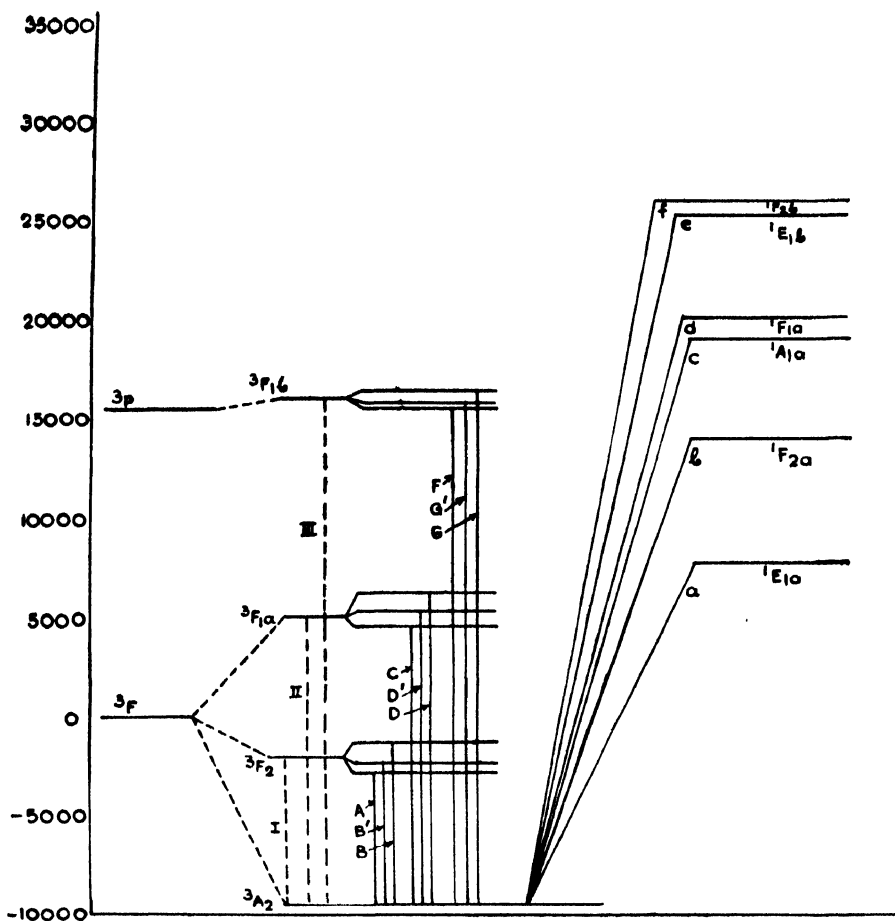
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In crystalline electric field of symmetry O_h , the 3F groundstate of the Ni^{2+} ion is split into three components 3A_2 , 3F_2 , ${}^3F_{1a}$ with successively increasing energy. In considering the absorption spectra, the transitions to the upper 3P level as also the forbidden transition to the singlets 1D , 1G and 1S with low transition probabilities should be taken into account. All these transitions have energies of the order of 10^4 cm^{-1} and since they take place only in combination with suitable vibrational transitions, the intensities of the light absorptions must be lower than if they had been due to pure electronic transitions. The three main transitions ${}^3A_2 \rightarrow {}^3F_2$, ${}^3A_2 \rightarrow {}^3F_{1a}$ and ${}^3A_2 \rightarrow {}^3F_{1b}$ (3P) give rise to broad bands called hereafter I, II and III over which the other weaker lines are superimposed.

For the aqueous solutions of several hydrated salts of Ni^{2+} , Dreisch *et al.* (1937, 1939) found that the peak of band I lies at 8300 cm^{-1} , peak of band II at 14100 cm^{-1} and peak of band III at 25000 cm^{-1} . This has been confirmed by Hartmann and Muller's (1958) observation of the absorption spectra of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ crystals. Hartmann and Muller (1958; cf. Mookherjee *et al.* 1960) have been able to resolve the bands II and III into several peaks, e.g., band II into three peaks *C*, *D*, *E* of more or less the same intensity and *a* of much smaller intensity; band III into two peaks *F*, *G* of nearly the same intensity as the peaks of II, and three other *b*, *c* and *d* of much smaller intensity. They obtained further two more very weak peaks *e*, *f* near 39000 cm^{-1} . They could apparently explain all these peaks *except E*, on the basis of the splitting of the different states of the Ni^{2+} ion caused by a small tetragonal field superimposed upon cubic field (Fig. 1.).

Since the intensity of this band *E* is almost equal to the transitions from other Stark levels, it cannot be due to any intercombination between terms of different multiplicity (Orgel 1955). Contention of Ballhausen (1955) and Hartmann and Muller (1958) that the occurrence of this band is due to (L.S.) coupling effect has been also contradicted by Jorgensen (1958). On the other hand, Mookherjee

et al (1960) have shown that the observed anisotropy of Ni^{2+} ion : $K_{\perp} - K_{\parallel} = 354 \times 10^{-6}$, assuming a tetragonal field, does not agree with the splitting $C \rightarrow D \approx 300$



Energy level diagram of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ion under cubic and orthorhombic field.
(Not drawn to scale)

cm^{-1} but with the splitting $C \rightarrow E \approx 1300 \text{ cm}^{-1}$. In that case the peak D remains unexplained. Paramagnetic resonance studies of several salts of Ni^{2+} by Griffiths and Owen (1952) show that the electric field in all these salts has really an orthorhombic symmetry. We have therefore assumed an orthorhombic field in all these salts and been able to prove that all the three peaks C , D and E are really due to transitions from ground $3A_2$ level to the three components of the level $3F_{1a}$ split up by the orthorhombic field.

We have neglected the effect of the spin-orbit interaction, which being a second order effect, is not so important in the case of optical absorption of Ni^{2+} ,

6H₂O complex and the inclusion of this in the Hamiltonian would unnecessarily complicate the present calculations, meant to explain the existing experimental facts, as far as they go.

Following the method of Van Vleck (1932), and Schlapp and Penney (1932), Tanabe and Sugano (1954), Pryce and Runciman (1958) and taking into consideration all the energy states as already mentioned, we have calculated the energy levels of Ni²⁺, 6H₂O with the following cubic and orthorhombic field parameters (Table I), and compared them with the experimental values obtained by the aforementioned authors. All things considered the fit is much better than that obtained by Hartmann and Muller. Authors have also worked out a complete theory of the susceptibility of Ni²⁺ ion in an orthorhombic field which will be discussed in a future communication.

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TABLE I

Cubic field parameter $Dq = 810 \text{ cm}^{-1}$
 Orthorhombic field parameters $\sigma = -70 \text{ cm}^{-1}$, $\delta = 20 \text{ cm}^{-1}$
 Racah parameters $B = 1030 \text{ cm}^{-1}$, $C = 4850 \text{ cm}^{-1}$

Splittings	Calculated values $\times 10^{-3} \text{ cm}^{-1}$.	Experimental values $\times 10^{-3} \text{ cm}^{-1}$.
${}^3A_2 ({}^3F) \rightarrow {}^3F_2 ({}^3F)$	7.957 (A)	
	8.010 (B') I	8.300
	8.097 (B)	
$\rightarrow {}^3F_{1a} ({}^3F)$	14.130 (C)	13.900
	14.405 (D) II	14.200
	15.423 (E)	15.200
$\rightarrow {}^1E_{1a} ({}^1D^1G)$	17.230 (a)	17.500
$\rightarrow {}^1E_{2a} ({}^1D^1G)$	24.811 (b)	23.900
$\rightarrow {}^3F_{1b} ({}^3P)$	25.030 (F)	
	25.080 (G') III	25.400
	25.120 (G)	
$\rightarrow {}^1A_{1a} ({}^1D^1G)$	26.941 (c)	26.900
$\rightarrow {}^1F_1 ({}^1D^1G)$	30.160 (d)	30.050
$\rightarrow {}^1E_{1b} ({}^1D^1G)$	35.879 (e)	
$\rightarrow {}^1F_{2b} ({}^1D^1G)$	36.399 (f)	39.000
$\rightarrow {}^1A_{1b} ({}^1S)$	67.929 (g)	—

REFERENCES

- Ballhausen, C. J., 1955, *C. J. Kgl. Danske Videnskab., Selskab, Mat, fys. Medd.* No. 8
29.
- Draisch, Th. and Kallscheuer, O., 1939, *Z. Phys. Chem.*, B45, 19.
- Griffiths, J. H. and Owen, J., 1952, *Proc. Roy. Soc., A*, **213**, 451.
- Hartmann, H. and Muller, H., 1958, *Disc. Farad. Soc.* **26**, 49.
- Jorgensen, C. K., 1958, *Disc. Farad. Soc.*, **26**, 90.
- Mookherji, A. and Chhonkar, N. S., 1960, *Ind. J. Phys.*, **43**, 363.
- Orgel, L. E., 1955, *J. Chem. Phys.*, **23**, 1004.
- Pryce, M. H. L. and Runcimann, W. A., 1958, *Disc. Farad. Soc.*, **26**, 34.
- Schalpp, R. and Penney, W. G., 1932, *Phys. Rev.*, **42**, 666.
- Tanabe, Y. and Sugano, S., 1954, *Proc. Phys. Soc. Japan*, **9**, 753, 766.
- Van Vleck, J. H., 1932, *Phys. Rev.*, **41**, 208.