

OPTICAL ABSORPTION OF Co^{2+} DOPED NH_4Cl : PHASE TRANSFORMATION STUDIES

BY P. A. NARAYANA

(*Department of Physics, Indian Institute of Technology, Kanpur, India*)

AND

PUTCHA VENKATESWARLU, F.A.S.C.*

(*Department of Physics, University of California, Santa Barbara, California*)

Received February 11, 1970

ABSTRACT

The absorption spectrum of Co^{2+} doped NH_4Cl has been studied from the room temperature to the liquid nitrogen temperature. A sudden change in the spectrum is observed between 243° K and 233° K which is attributed to the phase transition in the crystal. From the observed spectrum it is suggested that Co^{2+} goes in interstitially as well as substitutionally. Both the types of centers exist at room temperature, but with decrease in temperature substitutional ions migrate to interstitial sites, the process being stimulated at the phase transformation point so that the 77° K spectrum seems to be mostly due to the interstitial centers. The 77° K spectrum is analyzed in the approximation of octahedral symmetry for interstitial ions and the band positions are fitted fairly well with $B = 870 \text{ cm}^{-1}$ $Dq = 850 \text{ cm}^{-1}$ and $C = 4.4 B$. A blue shift of about 100 cm^{-1} is observed for ${}^4\text{T}_1(\text{P})$ band at the phase transition which is attributed to the increase in Dq value with the anomalous lattice contraction at the phase transition. The decrease in the lattice parameter calculated from this blue shift is around 0.4% which is in good agreement with the results of X-ray measurements. Two possible models for the interstitial complex are examined and the one with fourfold chlorine co-ordination associated with two neutral water molecules at the first neighbour (NH_4^+) site lying along $\langle 100 \rangle$ direction is suggested to be more probable.

INTRODUCTION

THE behavior of divalent transition metal ion impurities in ammonium halides has been found to be interesting by a number of earlier workers.¹⁻⁸ Mn^{2+} and Cu^{2+} are proposed to go interstitially in NH_4Cl having tetragonally

* On leave of absence from the Indian Institute of Technology, Kanpur, India.

distorted octahedral symmetry.¹⁻⁴ This preference for the interstitial entry as against the substitutional entry has been attributed to the relative stability of the octahedral complexes of these ions.¹ Practically no optical absorption studies of doped ammonium halides have been reported and emphasis has been laid on the paramagnetic resonance studies only.²⁻⁴ Since the paramagnetic resonance studies are not very convenient in the case of $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ as no EPR signal can be obtained at room temperature owing to a very short relaxation time, optical studies are undertaken to investigate this system. Moreover as NH_4Cl has disorder to order transformation and an anomalous lattice contraction⁵ at 243° K, it was felt desirable to investigate the effect of phase transformation on the optical absorption spectrum.

Ammonium chloride has CsCl structure at room temperature as well as at low temperature. The phase transformation at 243° K results in only an ordered orientation of NH_4^+ . In general, there are two possible sites for the impurity metal ions in the lattice, substitutional and interstitial on <100> axis in the space between the NH_4^+ ions. In the former case the site symmetry of the ion is body-centered cubic (b.c.c.) while in the latter case it should be tetragonally distorted octahedral as is found in the case of Mn^{2+} and Cu^{2+} in NH_4Cl ¹⁻⁴ as well as in the case of Ni^{2+} in NH_4Cl .^{2,5} From the EPR studies on $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ Zaripov and Chirikin² concluded that Co^{2+} has tetragonal site symmetry but nothing was said about its co-ordination. In fact in the EPR studies unless the superhyperfine structure is observed, it is difficult to distinguish between the interstitial and substitutional complexes as both can exhibit an overall tetragonal symmetry. The tetragonal distortion in the substitutional case may be caused by the presence of charge compensating cation vacancies lying along <100> direction. From the observed superhyperfine structure in $\text{ND}_4\text{Cl}:\text{Cu}^{2+}$ ¹⁰ and $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ ⁷ it could be concluded that the ion occupies interstitial position. Such studies are difficult to be carried out on $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ at room temperature, as pointed out earlier. On the other hand, optical studies are suitable in the present problem since the optical spectra are very sensitive to the b.c.c. and octahedral symmetries¹¹ and are relatively insensitive to the lower symmetry distortions of the cubic fields. Since the sign of the parameter Dq changes as one passes from the octahedral co-ordination to the b.c.c. co-ordination, the spectra expected in the two symmetries will be distinctly different from one another.

EXPERIMENTAL

The crystals were grown at room temperature from an aqueous solution of NH_4Cl containing 1% of CoCl_2 with 10% of urea added. The amount of

CoCl_2 added is varied from 0.5 to 20 mole per cent. The crystals grow along $\langle 100 \rangle$ direction. The presence of urea stimulates the cubic growth of the crystals, but does not contaminate them. The neutron diffraction studies of Levy and Peterson¹² confirm the absence of urea in NH_4Cl crystals grown in the presence of urea. The crystals grown are clear, pink in color and are in the form of good cubes. The spectra were recorded in the 293° K to 77° K range with a Cary-14 spectrophotometer. The error in the wavelength measurements of the band maxima is probably about $\pm 7 \text{ \AA}$. The temperature measurements are done with a Chromel Alumel thermocouple and a Leeds and Northrup potentiometer. The temperature of the crystal could be measured to better than $\pm 3^\circ \text{ K}$.

RESULTS

The crystals are analyzed spectrochemically for the quantitative determination of cobalt content. It is found that up to 5 mole per cent of the dopant added only 20% of the added quantity entered the lattice and when the dopant added is from 5 to 10 mole per cent, only 10% of the added quantity entered the lattice. If the dopant added is increased beyond 10 mole per cent, the amount of impurity entering the lattice has not changed appreciably from the amount entered when 10 mole per cent is added to the growth solution. As the amount of impurity added is increased beyond 20 mole per cent to the growth solution good crystals could not be obtained. The spectra of six crystals having different concentrations from 0.07 to 1.0 mole per cent are recorded. Except for a change in the intensity with the change in concentration in accordance with the results of spectrochemical analysis, the spectra are identical. The crystals are also examined under microscope and no visible clustering could be detected. For the present work a crystal containing 0.13 mole per cent of Co^{2+} , having a thickness of 0.6 cm., is chosen. The observed spectrum consists of two main bands named Q and R for convenience along with a few additional weak bands. The positions of these bands in wavenumbers are given in Table I. The bands Q and R which lie at about 16000 cm^{-1} and 19000 cm^{-1} respectively are shown in Fig. 1 at 77° K and 293° K. A third band P expected around 7400 cm^{-1} in the infrared region is masked by the absorption present in pure NH_4Cl , presumably due to $(\text{NH}_4)^+$ vibrations. This absorption could not be eliminated as perfect matching could not be obtained. The spectra of these crystals (in the form of pellets) recorded on a Perkin Elmer 521 spectrophotometer showed bands in the region 4000-3000 cm^{-1} characteristic of H_2O molecules.¹³ The R band consists of two main peaks R_1 and R_2 at 293° K (see Fig. 1). On cooling the crystal the R_2 peak decreases in intensity so that at 77° K only the R_1 peak

TABLE I

The positions and assignments of the bands observed in the absorption spectrum of $\text{Co}^{2+}:\text{NH}_4\text{Cl}$ at 77°K

Absorption peak	Observed position* (cm. $^{-1}$)	Assignment† ${}^4\text{T}_1(\text{F}) \rightarrow$	Calculated energy‡ (cm. $^{-1}$)
P	..	${}^4\text{T}_2(\text{F})$	7 420
Q	15 620	${}^4\text{A}_2(\text{F})$	15 910
	16 720	${}^2\text{T}_2(\text{G})$	16 380
R ₁	19 420	${}^4\text{T}_1(\text{P})$	19 380
	20 490	${}^2\text{T}_1(\text{H})$	20 520
	26 000	${}^2\text{T}_1(\text{H})$	25 650

* The peak of the R₂ band assigned to ${}^4\text{A}_2(\text{F}) - {}^2\text{T}_4(\text{P})$ transition of the substitutional Co^{2+} is at 18 320 cm. $^{-1}$ at the room temperature. It is not included in this table as it does not exist at 77°K .

† The assignments correspond to the levels of the interstitial Co^{2+} (octahedral co-ordination).

‡ Calculated in octahedral approximation with $B = 870$ cm. $^{-1}$, $Dq = 850$ cm. $^{-1}$ and $C = 4 \cdot 4 B$.

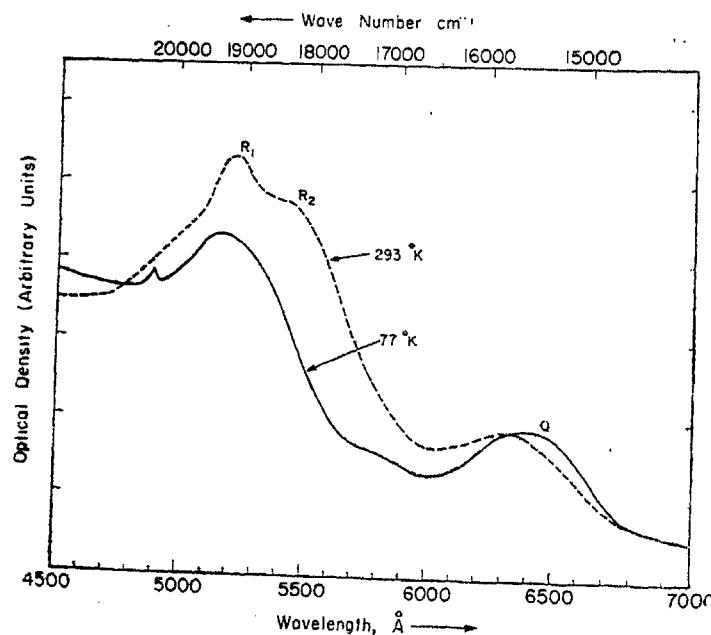


FIG. 1. The absorption spectrum of $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ at 293°K and 77°K . The broken line curve is for 293°K and the full line curve is for 77°K .

persists while R_2 nearly disappears. A blue shift of about 200 cm.^{-1} is observed for R_1 while going from 293° K to 77° K . The integrated intensity of the R band decreases on cooling. As against this the Q band shows an increase in intensity on cooling to 77° K as is evident from Fig. 1. At 77° K three weak bands appear at 16720 cm.^{-1} , 20490 cm.^{-1} and 26000 cm.^{-1} respectively, the first of which is broad while the second one is sharp.

To study the effect of phase transition, the temperature was decreased in steps from 293° K to 77° K . An abrupt change in the spectrum was observed between 243° K and 233° K as is shown in Fig. 2. The intensity of the R_2 peak shows a sudden decrease in this temperature region and in fact the peak disappears, whereas the integrated intensity of the Q band shows an increase. The R_1 peak is seen to have a large shift towards blue by about 100 cm.^{-1} . Figure 3 shows the variation of the band maxima of the two bands Q and R with temperature.

DISCUSSION

One of the interesting features of the present investigation is the disappearance of the R_2 peak on cooling, particularly in the range of the transition temperature. Such peaks whose intensities decrease on cooling are normally considered to be transitions from some excited level of the ground state whose depopulation on cooling results in a decrease in intensity, but such an explanation based on thermal depopulation does not seem to be true in the present case as it cannot explain the sudden decrease in intensity in the 10° K range around the transition temperature. Moreover the separation between R_1 and R_2 peaks is 1000 cm.^{-1} which is too large to consider R_2 as arising due to a transition from some excited vibrational level* of the ground state. The appearance of such a second peak is typical of the present system and has not been observed earlier in any other Co^{2+} spectra.

Another interesting feature is the increase in intensity of the Q band on cooling as against the decrease in intensity, normally observed for crystal field bands. The crystal field bands are generally vibronic in nature¹⁴ and the freezing of vibrations at low temperatures is expected to result in a decrease of the band intensities. The decrease in the overall intensity of the R band is in line with this argument.

* The Boltzmann factor for a level, if any, at 1000 cm.^{-1} will be too small to have it populated enough at room temperature to show any appreciable absorption.

A possible explanation to these anomalies appears to be the existence of two types of Co^{2+} centers in the crystal called C_1 and C_2 for convenience; C_1 and C_2 being responsible respectively for the R_1 and R_2 peaks. Both the types of centers exist at room temperature, although from the relative intensities of R_1 and R_2 bands, the number of C_1 centers seem to be larger. On cooling the crystal the C_2 type of centers get transformed to C_1 type of centers and the process seems to be somehow stimulated at the phase transformation. As a result of this, the number of C_2 type of centers at 77° K becomes very small, resulting in the disappearance of the R_2 peak and the 77° K spectrum seems to be predominantly due to the C_1 type centers. Since both C_1 and C_2 type centers have absorption lines in the region of the R band, the integrated intensity of this band depends on the total number of C_1 and C_2 centers and hence follows a simple decrease in intensity pattern on cooling although C_2 type of centers get converted to C_1 type. There is probably no band due to C_2 type of centers in the region of the Q band since otherwise this band should also have shown features similar to the R band. The Q band seems to be due to only the C_1 type of centers and hence shows an increase in intensity with increase in the number of C_1 type of centers, on cooling. In fact, there should be two mutually opposite factors controlling the intensity of this band, the freezing of vibrations trying to decrease the intensity of this band and the increase in C_1 centers trying to increase the intensity. This argument is supported by the observation that there is a sudden increase in intensity of this band at the phase transition while its intensity increases

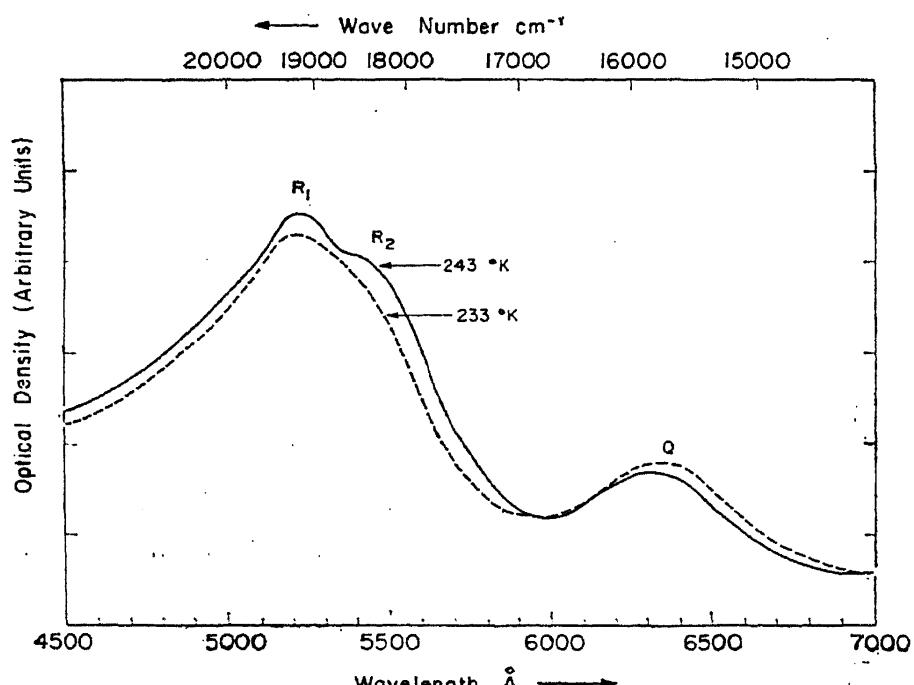


FIG. 2. The absorption spectrum of $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ before and after the phase transition. The broken line curve is for 233° K and the full line curve is for 243° K.

only slightly as one goes from 233° K to 77° K, indicating thereby the balancing of the two factors in this temperature region.

Since the 77° K spectrum seems to be only due to the C_1 centers, we shall now investigate the possible co-ordination for such centers. The two likely co-ordinations for Co^{2+} in NH_4Cl as mentioned earlier are b.c.c. and octahedral corresponding respectively to the substitutional and interstitial centers. We shall not consider the distortion of cubic symmetry by charge compensation vacancies at present. The spectrum of Co^{2+} in octahedral symmetry has been extensively studied and the general features are now well understood.¹⁸⁻¹⁵ The only body-centered cubic spectrum of Co^{2+} reported is by Stahl-Brada and Low in CaF_2 ,¹⁹ where the Dq value is found to be very low compared to the values known in octahedral co-ordinations. The energy levels of Co^{2+} in b.c.c. and octahedral co-ordinations are shown in Fig. 4, for the values of the parameters discussed later. Three intense spin allowed transitions are expected in the two cases but their positions should be markedly different. In both the co-ordinations a band is expected around 19000 cm^{-1} , in the region of the R band corresponding to the transition ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ in

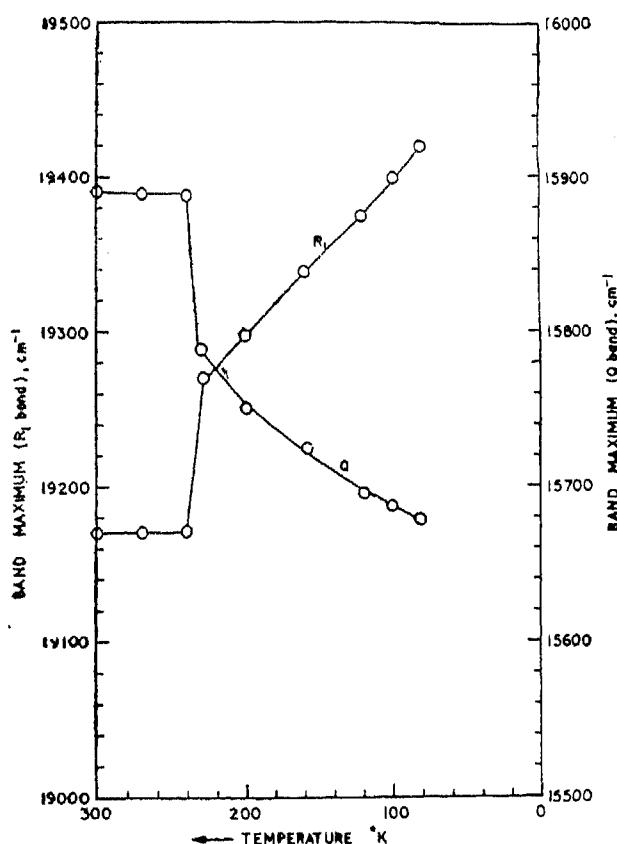


FIG. 3. The variation of the band maxima with temperature for $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ (a) Q band, ${}^4\text{T}_1(\text{F}) \cdots {}^4\text{A}_2(\text{F})$ and (b) R₁ band, ${}^4\text{T}_1(\text{F}) - {}^4\text{T}_1(\text{P})$.

the b.c.c. symmetry and 4T_1 (F) \rightarrow 4T_1 (P) in the octahedral symmetry. However in the region of the Q band around 16000 cm.^{-1} , only 4A_2 (F) level belonging to the octahedral symmetry is expected to lie. No quartet level of b.c.c. symmetry is expected to be in this region. If the level 4T_1 (F) of b.c.c. were to lie in this region, one would expect a large value for the parameters B or Dq, which would be quite unlikely. It was not possible to find any reasonable values for the set of parameters B and Dq with which all the observed bands could be fitted even approximately in the b.c.c. symmetry. On the other hand on the basis of octahedral coordination for C_1 centers, all the observed bands could be explained reasonably well. The two intense bands Q and R can be readily assigned to the transitions to the levels 4A_2 (F) and 4T_1 (F) respectively. The observed weak bands are also typical of octahedral co-ordination. A broad weak band is observed in most of the octahedral complexes around 17000 cm.^{-1} ¹⁶ and such a band has been observed at 16720 cm.^{-1} (see Fig. 1) in the present case which is assigned to the transition to the 2T_2 (G) level. The sharp weak band at 20490 cm.^{-1} (in Fig. 1) is assigned to the 2T_1 (H) level and is again very typical of octahedral complexes and its structure has been studied in considerable detail by Pappalarado.¹⁶ The weak band obtained at 26000 cm.^{-1} but not shown in the figures is assigned to the 2T_1 (H) level.

The energies of the three spin allowed transitions involve the parameters B and Dq only and a good fit with the observed energies is obtained with $B = 870\text{ cm.}^{-1}$ and $Dq = 850\text{ cm.}^{-1}$. The calculated energy levels are shown in Fig. 4. The energies of the spin forbidden levels involve the electrostatic parameter C besides B and Dq. Keeping B and Dq constant, as obtained from the spin allowed transitions, the value of C is obtained by fitting with the sharp 2T_1 (H) band at 20490 cm.^{-1} and the value so obtained is given by $C = 4.4 B$. The calculated energies of the other doublet levels turn out to be 16380 cm.^{-1} and 25650 cm.^{-1} which are quite close to the observed bands at 16720 cm.^{-1} and 26000 cm.^{-1} respectively.

We shall now discuss the possible co-ordination for C_2 centers. An octahedral co-ordination for these centers seems to be unlikely since in that case one expects a band due to them in the region of the Q band similar to the R_2 line which is not the case. The possibility that the absorption of both the centers C_1 and C_2 overlap giving only one peak for the Q band does not appear to be likely as in such a case the intensity of the Q band should not increase as observed while going through the transition temperature. The C_2 centers are probably substitutional ions having approximately b.c.c. symmetry. Assigning the R_2 peak to the 4A_2 (F) \rightarrow 4T_1 (P) transition in the b.c.c. symmetry and

taking the same value of B , *viz.* 870 cm^{-1} , as found for C_1 centers, we get a Dq value of 420 cm^{-1} . The other two quartet levels $^4T_1(F)$ and $^4T_2(F)$ will then be expected at 7300 cm^{-1} and 4200 cm^{-1} which are far below the region of the Q band. The $^4T_1(F)$ band should be around the region of the P band but nothing could be said definitely about it owing to the strong absorption of the host crystal in that region. The intensity of the $^4T_2(F)$ band is expected to be very low as is observed by Stahl-Brada and Low¹⁹ in the case of $CaF_2:Co^{2+}$. In tetrahedral co-ordination also the intensity of such a band is found to be low.²⁰ Probably due to these reasons no prominent features corresponding to these two bands of C_2 centers could be observed.

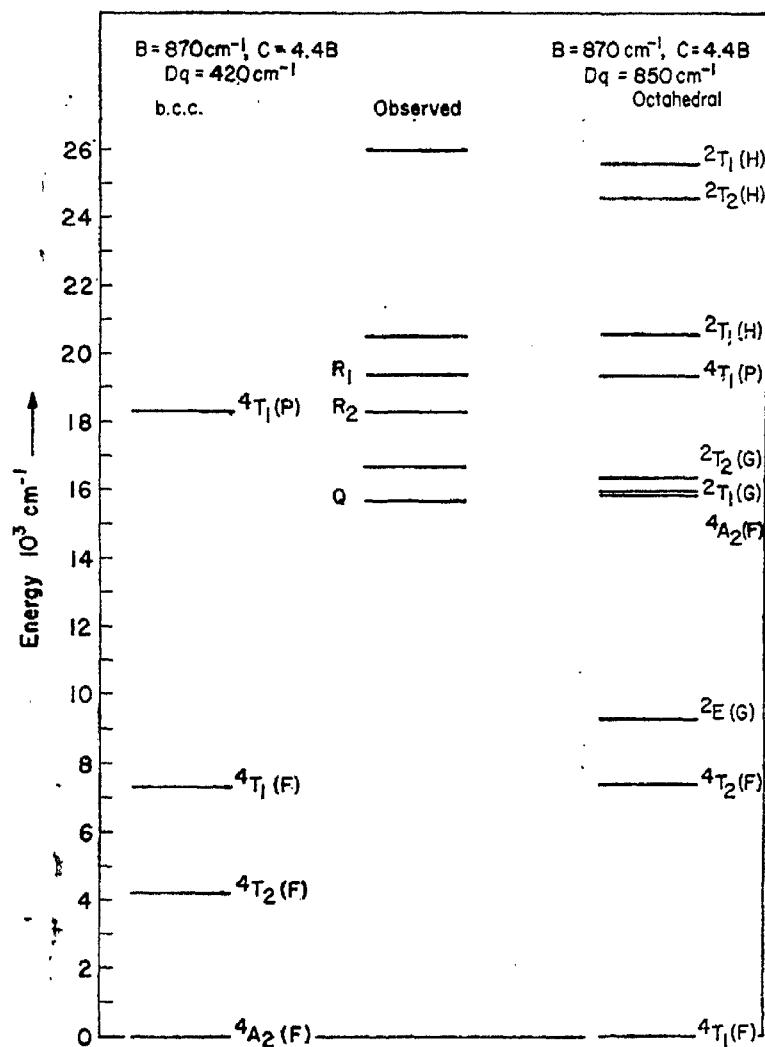


FIG. 4. The energy levels of Co^{2+} in the body-centered cubic and octahedral symmetries. Only the quartet levels are shown in the body-centered cubic symmetry.

One of the likely processes for the conversion of b.c.c. type C_2 centers to octahedral type C_1 centers may be given as follows. There should be two potential wells available for Co^{2+} in the crystal at substitutional and interstitial

A 2

positions corresponding to the C_2 and C_1 centers respectively. The potential well at the substitutional site is perhaps shallower as indicated by the lesser number of C_2 centers compared to the number of C_1 centers at room temperature. With a sudden increase in the crystal field strength due to anomalous lattice contraction at the phase transformation, the shape and depth of this well probably changes suddenly and a tunnelling of ions to the adjoining deeper well of the more stable interstitial site may take place resulting in a sudden increase in the number of C_1 centers and decrease in the number of C_2 centers. This possibility of structural changes for Co^{2+} ion in the present case is not very unusual as Cotton and Holm²¹ have also suggested the possibility of structural changes to explain their results of magnetic measurements on some Co^{2+} complexes.

The sudden increase of the crystal field strength at the phase transformation is indicated by the blue shift of the R_1 peak. The upper level of this peak is $^4T_1(P)$ whose energy increases with an increase in Dq value. The sudden increase in the energy of R_1 peak should therefore correspond to a sudden increase in the Dq value or crystal field strength at the phase transformation. Attributing the observed blue shift of 100 cm.^{-1} during the phase transition to an increase in Dq only, an increase of about 2% in Dq value is calculated. Assuming a simple $1/R^5$ dependence of Dq where R is the metal-ligand distance, one finds that R decreases by about 0.4%. This is in good agreement with the decrease of 0.5% in the lattice parameter inferred from X-ray data.⁹ It has been observed that even below phase transformation point the R band maximum continues to shift towards shorter wavelengths (see Fig. 3). This is probably because the lattice parameter of NH_4Cl continues to decrease below the phase transition.

According to the present observations the phase transition in $\text{NH}_4\text{Cl}:\text{Co}^{2+}$ is around 238° K while in pure NH_4Cl it has been found to be around 243° K . This difference if real is perhaps due to the probable effect of impurities in shifting the transition temperature and a similar shift in the transition temperature has been observed by Sastry and Venkateswarlu⁷ in $\text{NH}_4\text{Br}:\text{Cu}^{2+}$.

The C_1 center which involves a substitutional Co^{2+} introduces an extra positive charge while the C_2 center which involves an interstitial Co^{2+} introduces two extra positive charges. The charge neutrality can be achieved by the creation of one first neighbor NH_4^+ vacancy in the case of C_1 center and two first neighbor NH_4^+ vacancies in the case of C_2 center. Since it is well known that NH_4Cl does not have water of crystallization the presence of water bands in the doped crystals can probably be well understood by assuming that

neutral water molecules occupy the first neighbor NH_4^+ vacancies near the Co^{2+} ions. Models of this kind have been proposed,¹ for Mn^{2+} , Cu^{2+} and Ni^{2+} in doped NH_4Cl .

An anomalous observation in the present work is the red shift of the Q band on cooling. On the basis of increase in Dq this band should have also shown an increase in energy. The observed red shift is perhaps to be explained by considering the change in the shape of the electronic energy surface of the excited state $^4A_2(F)$ with temperature, but the details are not yet well understood.

ACKNOWLEDGEMENT

The authors would like to express their thanks to Dr. A. K. Mehra for helpful discussions.

REFERENCES

1. Goode, D. H. .. *J. Chem. Phys.*, 1965, **43**, 2830.
2. Zaripov, M. M. and Chirikin, G. K. .. *Sov. Phys. Solid State (Eng. Trans.)*, 1966, **7**, 74.
3. ——— .. *Ibid.*, 1965, **6**, 1290; 1966, **7**, 2391 and 2744.
4. Pilborw and Spaeth, J. M. .. *Phys. Stat. Sol.*, 1967, **20**, 225.
5. Narayana, P. A. and Venkateswarlu, P. .. *J. Chem. Phys.*, 1970, **52**, 5159.
6. Sastry, M. D. and Venkateswarlu, P. .. *Mol. Phys.*, 1967, **13**, 161.
7. ——— .. *Proc. Ind. Acad. Sci.*, 1967, **66**, 208.
8. Forman, A. and Van Wyke, J. A. .. *Can. J. Phys.*, 1967, **45**, 3381.
9. Par Paul Dinehert .. *Helv. Phys. Acta*, 1939, **15**, 462.
10. Trappeniers, N. J. and Hagen, S. H. .. *Physica*, 1965, **31**, 122 and 251.
11. Ballhausen, C. J. .. *Introduction to Ligand Field Theory*, McGraw-Hill Book Co. Inc., New York, 1962.
12. Levy, H. A. and Peterson, S. W. .. *Phys. Rev.*, 1952, **86**, 766.
13. Herzberg, G. .. *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., Inc., New York, 1945,
14. Van Vleck, J. H. .. *J. Phys. Chem.*, 1937, **41**, 67.

15. Low, W. .. *Phys. Rev.*, 1958, **109**, 256.
16. Pappalarado, R. .. *Phil. Mag.*, 1959, **4**, 219.
17. —, Wood, D. L. .. *J. Chem. Phys.*, 1961, **35**, 2041.
and Linares, R. G., Jr.
18. Ferguson, J., Wood, .. *Ibid.*, 1963, **39**, 881.
D. L. and Knox, K.
19. Stahl-Brada and Low, .. *Phys. Rev.*, 1959, **113**, 775.
W.
20. Weakliem, H. A. .. *J. Chem. Phys.*, 1962, **36**, 2117.
21. Cotton, F. A. and .. *J. Am. Chem. Soc.*, 1960, **82**, 2979.
Holm, R. H.