Contribution from the Chemistry Department,
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

# The Low-Temperature Spectrum of $Co^{2+}$ in Cadmium Difluoride

By C. SIMO,[1a] E. BANKS, and S. HOLT[1b]

*Received January 27, 1969*

The optical spectrum of $Co^{2+}$ in $CdF_2$ is measured at 4.2°K. Absorption bands are found centered at 3750, 4720, 7250, and 18,750 $cm^{-1}$. Fine structure associated with vibrational and spin–orbit components is observed; $Dq$ and $B$ are obtained. Above 8 mol % (3.5 $M$ $Co^{2+}$ in $CdF_2$) the intensity-giving mechanism is seen to change from vibronic to static distortion.

## Introduction

In 1959 Stahl-Brada and Low reported on the spectrum of $Co^{2+}$ in $CaF_2$.[2] In this report they compared their experimental data with the results of a crystal field calculation which included spin–orbit coupling as well as the cubic potential term. Their measurements, at 80°K, produced spectra which exhibit somewhat unresolved fine structure. This fine structure was totally ascribed to spin–orbit components and spin-forbidden transitions. Preliminary measurements in this laboratory on $Co^{2+}$–$CdF_2$ indicated that for this cubic system the spectra were somewhat too complex to be so described and therefore deserved closer investigation. Further, an investigation of $Co^{2+}$–$CdF_2$ would provide an opportunity to compare the difference in crystal field strength for the two hosts concerned. Thirdly, it would give us the opportunity to check the possibility of noncubic contributions to the intensity-providing mechanism.

## Experimental Section

High-purity $CdF_2$ was prepared by the method of Abbruscato.[3] Crystals were grown using the Bridgman technique. This involved placing the $CdF_2$ and $CoF_2$ into a graphite crucible which was slowly lowered through the work coil of an induction heater. The crystal was then cooled from ~1100° to room temperature over a 30-hr period.

During the entire operation the crucible was protected from oxidation by maintaining a continuous flow of helium over it. Concentrations of 0.5–14.0 mol % $CoF_2$ were used. Cobalt concentrations, as the thiocyanate complex[4] were determined on chips of the crystals actually used for optical measurements. A typical crystal diameter for a 2 mol % sample was 7 mm. Crystal thickness was varied from 0.3 to 17 mm depending on the path length desired. No attempt was made to grow or to cut the crystals to any particular orientation as not only is the lattice a cubic one but preliminary experiments indicated no anisotropic optical behavior.

Optical measurements were obtained at 300, 80, and 4.2°K. Cooling a crystal to 80°K was accomplished by mounting the crystal in a holder which was in turn inserted into a cavity in a quartz dewar. The cavity was completely surrounded by liquid $N_2$. In addition, an amount of liquid nitrogen sufficient to come into contact with the base of the holder was allowed to enter the cavity.

For liquid helium measurements, crystals were mounted in a holder attached to a helium reservoir. The holder was so constructed that the liquid helium was able to circulate about the entire 360° circumference of the cylindrical crystal, separated from the crystal by only a thin brass wall. This apparatus was then placed in an evacuated, liquid nitrogen cooled cavity.

Measurements from 4000 to 20,000 Å were made using a Cary 14 recording spectrophotometer equipped with a high-intensity source. Measurements beyond 20,000 Å were made using a Perkin-Elmer 521 grating spectrophotometer and were made at room temperature only.

## Results

Figure 1 displays the room-temperature spectrum of the absorption bands of $Co^{2+}$–$CdF_2$ in the infrared region. These are undoubtedly transitions associated with the d-manifold of $Co^{2+}$ since measurements on several different crystals containing various concentrations of $Co^{2+}$, but all of the same thickness, show variations in intensity of these bands paralleling the concentration of $Co^{2+}$ in the crystals. The visible–near-ir spectra of $Co^{2+}$–$CdF_2$ at 298 and 77°K are shown in Figure 2 and at 4.2°K in Figure 3. These samples contained 0.5–1.8 mol % cobalt. At 4.2°K the two bands shown display partially resolved structure. The locations of these maxima and molar extinctions, calculated for the 0.5 mol % sample, are listed in Table I. The certainty of the positions of the maxima is probably no better than ±10 $cm^{-1}$ for the most pronounced peaks and may be no better than ±50 $cm^{-1}$ for the less well-resolved bands. Weaker bands, occurring above 22,000 $cm^{-1}$, are shown in Figure 4. These maxima certainly arise from transitions involving a change in spin multiplicity. Crystal field theory for the cobalt $d^7$ configuration in cubic, eightfold coordination adequately accounts for the appearance and relative positions of three major, parity forbidden, spin-allowed bands.

In preliminary observations the bands centered at 7500 $cm^{-1}$, ${}^4T_1(F)$, and 18,800 $cm^{-1}$, ${}^4T_1(P)$, were seen to decrease in area with decreasing temperature, Figure 2. This is indicative of vibronic contribution to the intensity. An approximate calculation of the frequency, $\nu$, of the vibration responsible was made using the relationship[5]

$$\log \frac{f + f_0}{f - f_0} = \frac{\Theta}{2.303T}$$

---

(1) (a) NSF–SDP Postdoctoral Fellow. (b) Author to whom correspondence should be addressed: Chemistry Department, University of Wyoming, Laramie, Wyo. 82070.

(2) D. R. Stahl-Brada and W. Low, *Phys. Rev.*, **113**, 775 (1959).

(3) V. M. Abbruscato, Ph.D. Thesis, Polytechnic Institute of Brooklyn, June 1967.

(4) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, N. Y., 1950, p 279.

(5) R. L. Carlin and J. Walker, *J. Chem. Phys.*, **46**, 3921 (1967).

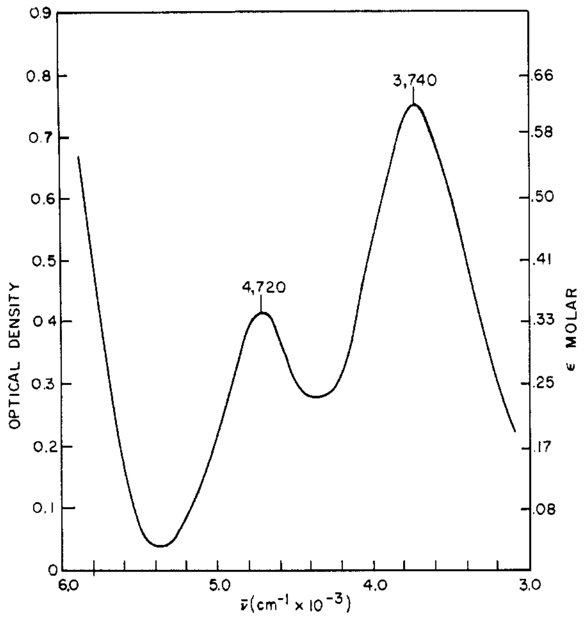

Figure 1.—Absorption spectrum of $Co^{2+}$–$CdF_2$ at room temperature in the infrared region; $l$ = 0.8 cm, 3.5 mol % $Co^{2+}$.

This is the slope–intercept form of the equation $f = f_0[1 + \exp(\Theta/T)]$,[6] in which $T$ is in degrees Kelvin and $\Theta$ is the energy of the spacing, $\Theta k = h\nu$, also in temperature units. The oscillator strength, $f$, was approximated by planimetric integration of the band, with the abscissa in energy units ($cm^{-1}$) and the ordinate in units of extinction, followed by the application of the equation $f = 4.32 \times 10^{-9} \int \epsilon \, d\nu$.[7] The values obtained appear in Table II. The order of magnitude of $\nu$ appears to indicate contribution by lattice vibration. The approximate value of $\nu$ is in agreement with an observed far-infrared absorption of $CdF_2$[8] but not in agreement with a recent determination of $\nu \simeq 150\ cm^{-1}$ for the 16,000–20,000-$cm^{-1}$ band of $Co^{2+}$–$CdF_2$.[9] A study of the variation of band intensity as a function of $Co^{2+}$ concentration as well as temperature has led to the observation that the area of the $^4T_1(F)$ band at 77°K was not always less than its area at room temperature. (See Figure 5.) The areas become equivalent; *i.e.*, evidence of vibronic contribution to intensity disappears, in the more heavily doped samples. Figure 6 contains a plot of oscillator strength of the $^4A_2 \rightarrow {}^4T_1(F)$ transition as a function of $Co^{2+}$ concentration.

## Discussion

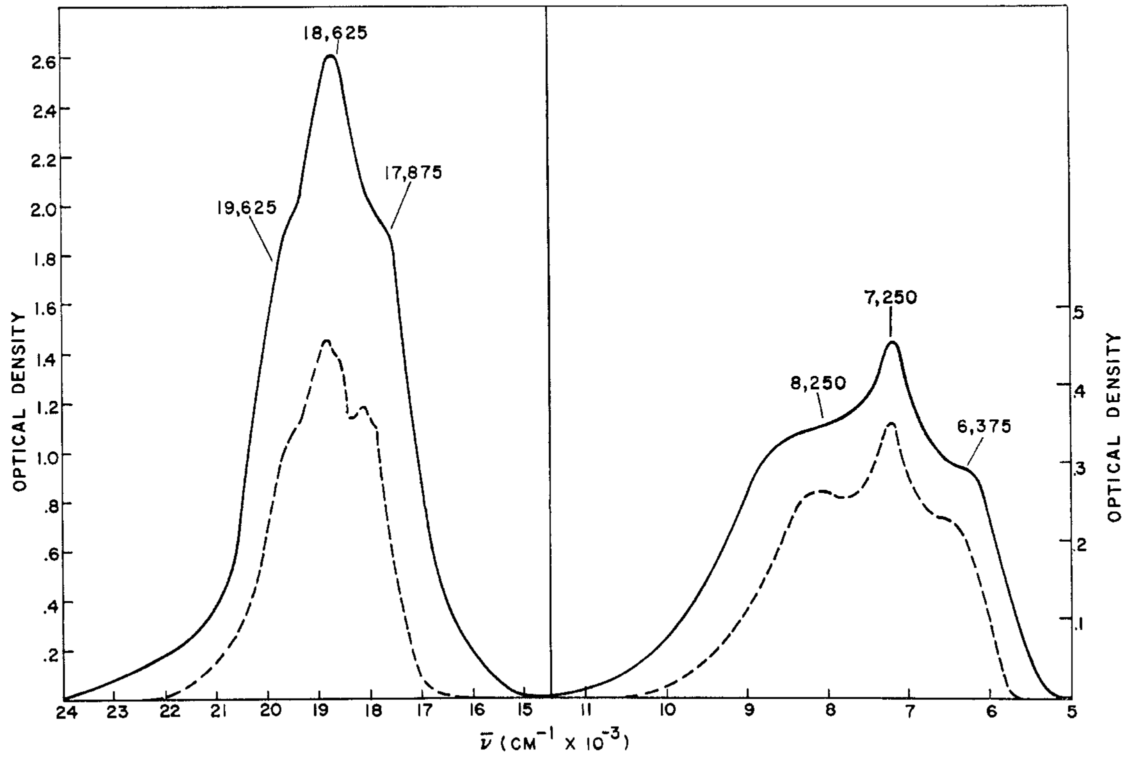

Figure 2.—Absorption spectrum of $Co^{2+}$–$CdF_2$ at 298°K (solid line) and 80°K (dotted line) in the visible–near-ir region. Values of optical density and extinction are given for the 0.5 mol %, 1.7 cm sample.

$CdF_2$ crystallizes with the fluorite structure. In this structure each $Cd^{2+}$ ion is surrounded by eight $F^-$ ions at the corners of a cube. Each $F^-$ ion is, in turn, the center of a tetrahedron of $Cd^{2+}$ ions. The point group is $O_h$, but the crystal field parameter $Dq$ has a sign opposite to that in a six-coordinated octahedral complex. The ground state of $Co^{2+}$ is $^4F_1$ which in a cubic field of four- or eightfold coordination gives rise to $^4A_2$, $^4T_2$, and $^4T_1$ levels in order of increasing energy. The higher energy $^4P$ gives rise to only one state, a $^4T_1$.[10] Ignoring the absorption at 4720 $cm^{-1}$, for the moment, assignment of the three bands centered at 3800, 7250,

---

(6) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(7) See, for example, T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, pp 276–280.

(8) D. R. Bosomworth, *Phys. Rev.*, **157**, 709 (1967).

(9) A. P. Smolov and Z. C. Yakovleva, *Soviet Phys.-Solid State*, **10**, 1513 (1968).

(10) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

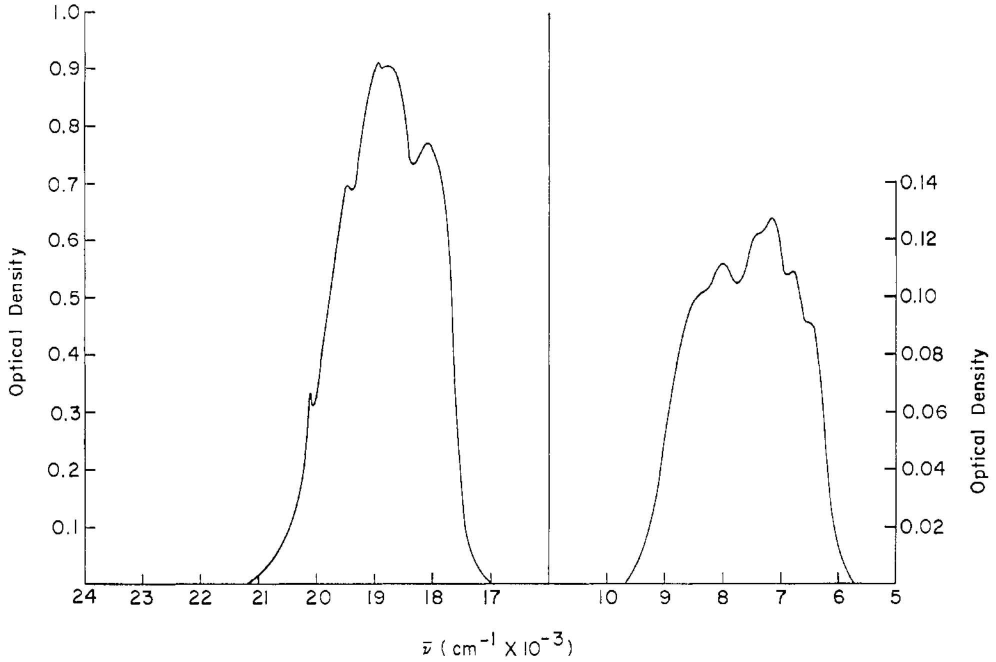

Figure 3.—Absorption spectrum of $Co^{2+}$–$CdF_2$ at 4.2°K in the visible–near-ir region.

Table I

Position of Absorption Maxima for the Visible and Near-Infrared Bands of 0.5 Mol % $Co^{2+}$ in $CdF_2$ at ~5°K

| Band II | | | Band III | | |
|---|---|---|---|---|---|
| $\nu$, cm$^{-1}$ | $\Delta\nu$, cm$^{-1}$ | $\epsilon$ | $\nu$, cm$^{-1}$ | $\Delta\nu$, cm$^{-1}$ | $\epsilon$ |
| 6450 | | 0.56 | 18,215 | | 2.16 |
| | 330 | | | 435 | |
| 6780 | | 0.74 | 18,850 | | 2.85 |
| | 360 | | | 285 | |
| 7140 | | 0.94 | 18,935 | | 2.85 |
| | 270 | | | 335 | |
| 7410 | | 0.91 | 19,510 | | 1.96 |
| | 590 | | | 565 | |
| 8000 | | 0.79 | 20,075 | | 0.84 |
| | 330 | | | | |
| 8330 | | 0.70 | | | |

Table II

Temperature Dependence of the Band Area of the $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ Transitions of $Co^{2+}$–$CdF_2$

| Band | $T$, °K | $10^6 f$ | Log $\frac{f+f_0}{f-f_0}$ | Θ, °K | $\nu$, cm$^{-1}$ |
|---|---|---|---|---|---|
| $^4A_2 \rightarrow {}^4T_1(F)$ | 300 | 27.1 | 0.55 | 76 | 53 |
| (1.8 mol % $Co^{2+}$) | 80 | 20.4 | 0.84 | | |
| | 4 | 15.2 | | | |
| $^4A_2 \rightarrow {}^4T_1(P)$ | 300 | 100.0 | 0.20 | 86 | 60 |
| (0.5 mol % $Co^{2+}$) | 80 | 41.5 | 0.54 | | |
| | 4 | 22.5 | | | |

and 18,750 cm$^{-1}$ as transitions from $^4A_2$ to $^4T_2(F)$, $^4Ti(F)$, and $^4T_1(P)$, respectively, is in reasonable agreement with observations and calculations of position and maximum separations due to spin–orbit coupling for $Co^{2+}$–$CaF_2$.[2,10] The details of the spectra raise several questions, however. Among these are: (1) What is the origin of the fine structure on the two higher energy manifolds? (2) What is the explanation for the 4720-cm$^{-1}$ absorption? (3) How can we explain the unusual intensity variations?

Figures 5 and 6 clearly show a change in the intensity-producing mechanism as a function of $Co^{2+}$ concentration. This can be explained in the following way. There is a distinct difference in ionic size between the $Co^{2+}$ ion and the $Cd^{2+}$ ion (0.72 *vs.* 0.97 Å). At low concentrations introducing the smaller $Co^{2+}$ ion into the lattice would be expected to have little effect upon the over-all lattice. This appears to be the case in the recent work of Smolov and Yakovleva.[9] They found that the intensity-giving mechanism for Co–$CdF_2$ is vibronic, as would be expected for $Co^{2+}$ in a cubic environment, and that the exciting vibration has a value of 150 cm$^{-1}$. This appears to be in agreement with a 160-cm$^{-1}$ vibrational mode observed in $CdF_2$ by Bosomworth.[8] The Russian workers did not report the exact concentration range in which they worked; however, they did state that the concentrations were comparable to those used by Stahl-Brada and Low, 0.1–0.3 mol %.

When the $Co^{2+}$ concentration has reached 0.5 mol %, a strictly vibronic mechanism is no longer sufficient to explain the variation of intensity with temperature. Determination of the value of the exciting vibration yields $\nu$ = 60 cm$^{-1}$ which, while it may correspond to a vibration of the $CdF_2$ lattice,[8] deviates too grossly from the value determined by the Russian workers[9] to be explained by a simple vibronic mechanism. This conclusion is further emphasized by the data obtained at higher concentrations of $Co^{2+}$, Figures 5 and 6.

The observed behavior is explainable in terms of a collapse of local cubic symmetry. When sufficient $Co^{2+}$ is introduced into the lattice, it appears that a local deformation may occur in $Co^{2+}$-rich areas to accommodate the small size of the $Co^{2+}$ ion. However, at the lower concentrations of $Co^{2+}$, not all $Co^{2+}$ ions are in noncubic sites. This is evidenced by the fact that there is a decrease in oscillator strength upon

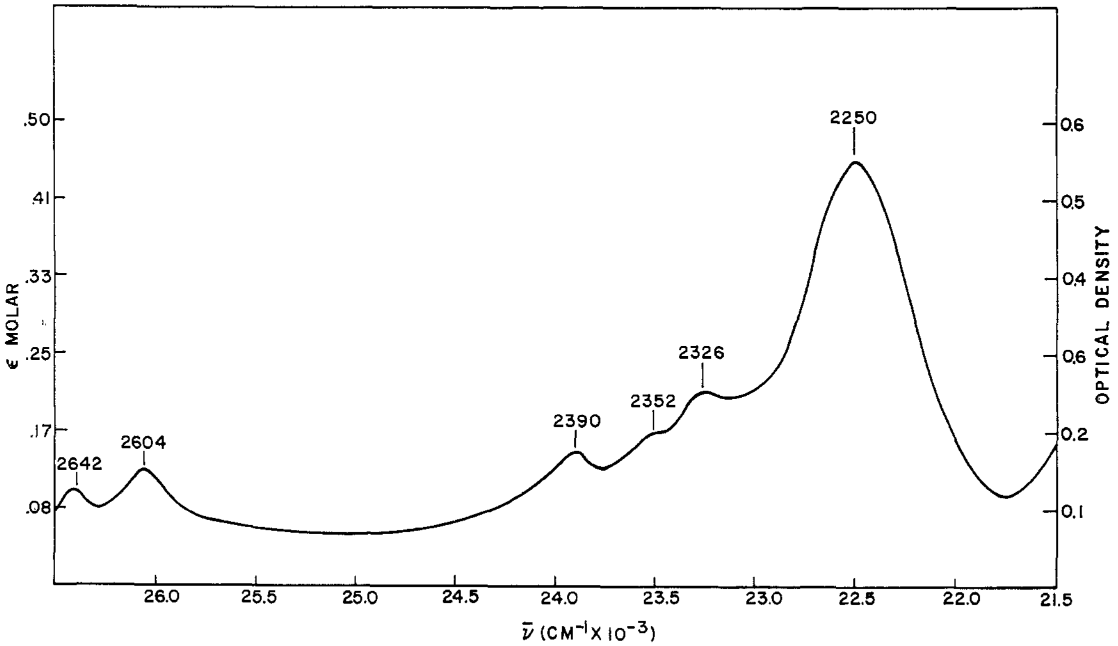

Figure 4.—Absorption spectrum of $Co^{+2}$–$CdF_2$ at 4.2°K; $l$ = 0.8 cm, 3.5 mol % $Co^{2+}$.

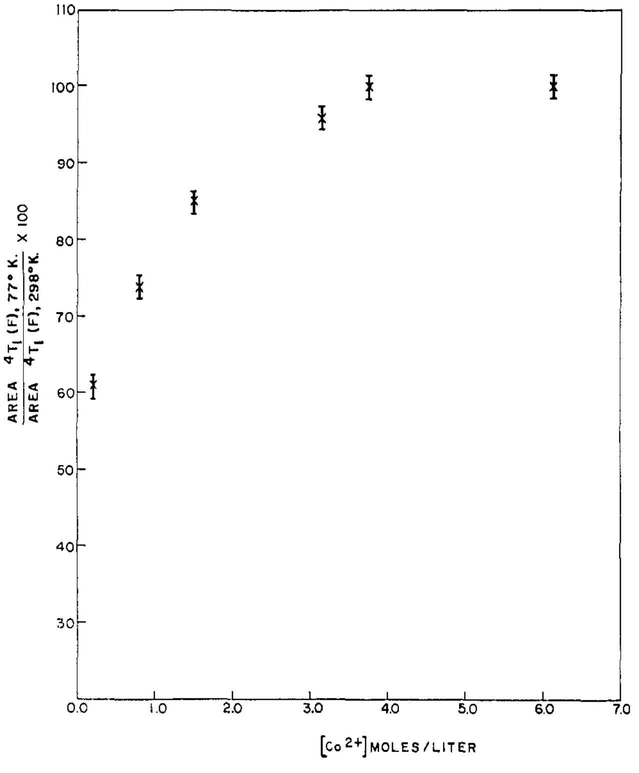

Figure 5.—Dependence of the difference in area of the $Co^{2+}$–$CdF_2$ $^4T_1(F)$ band at 77 and 298°K on $Co^{2+}$ concentration. The vertical lines indicate range of probable error.

cooling even in samples of 7 mol % cobalt. Above 7 mol % cobalt the intensity-giving mechanism is explainable wholly in terms of a static distortion.

It is tempting to use the observation of a static contribution to the intensity to help explain the fine structure on the visible and near-infrared bands and to rationalize the appearance of the maximum at 4720 $cm^{-1}$. Over-all, the optical spectrum of $Co^{2+}$–$CdF_2$ is similar to that of Co(II) in a tetrahedral field.[11,12]

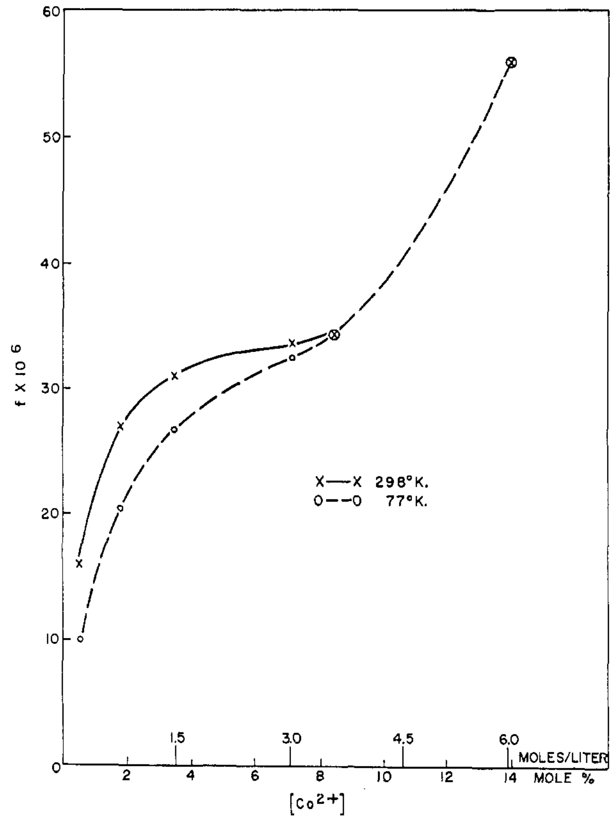

Figure 6.—The variation of oscillator strength of the $Co^{2+}$–$CdF_2$ $^4T_1(F)$ band with $Co^{2+}$ concentration.

The absorptions and fine structure, resolved at low temperature, of tetrahedral $Co^{2+}$ ($+Si^{4+}$) in garnets have been accounted for by a combination of lowered symmetry and spin–orbit coupling in which the noncubic is greater than the spin–orbit contribution.[12]

---

[11] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

[12] D. L. Wood and J. P. Remeika, *J. Chem. Phys.*, **46**, 3595 (1967).

Here the $^4T_2$ level (4680–4980 $cm^{-1}$) is split into two bands in the infrared region, $^4E$ and $^4B$, with ∼250 ± 50 $cm^{-1}$ separation. This splitting is analogous to that which we observe here, although much less in magnitude, indicating perhaps a larger noncubic contribution in the $Co^{2+}$–$CdF_2$ system than in the garnets.

**Transition $^4A_2 \rightarrow {}^4T_2(F)$.**—From the position of the lowest absorption band we estimate *Dq* to be ∼380 $cm^{-1}$. This leads to a value of $B' = 972\ cm^{-1}$, which is slightly greater than the measured free-ion value of 970 $cm^{-1}$.[13] This, of course, only reflects the fact that the original values substituted into the Tanabe–Sugano equations were obtained from very broad bands. For example a $B'$ value of ∼870 $cm^{-1}$ is obtainable for $Co^{2+}$–$CdF_2$ if the shoulders at 6450 and 18,000 $cm^{-1}$ are assumed to be the electronic origins of the two broad bands. As one might expect, in a system which contains fluoride ion as the ligand, these values of $B'$ indicate very little covalence.

Comparison of the *Dq* value obtained from measurements on this system, 380 $cm^{-1}$, and the *Dq* obtained for $Co^{2+}$–$CaF_2$(2), 340 $cm^{-1}$, indicates a surprisingly large difference in energy when one takes into account that there is only 0.02-Å difference between the ionic radii of $Cd^{2+}$ (0.97 Å) and $Ca^{2+}$ (0.99 Å).[14] The relatively low *Dq* of both $Co^{2+}$–$CdF_2$[15] is undoubtedly caused by the difference between the ionic radius of the $Co^{2+}$ ions (0.72 Å)[16] and that of the ion for which it is substituted. Variation in *Dq* between the $Ca^{2+}$ and $Cd^{2+}$ hosts, on the other hand, must be a specific reflection of altered nearest neighbor polarizations, perhaps in an obvious way. In fact, evidence has been obtained recently[8,17] that $Cd^{2+}$ probably participates in a greater degree of covalent bonding than $Ba^{2+}$, $Sr^{2+}$, or $Ca^{2+}$ in the alkaline earth fluorides.

**Transitions $^4A_2 \rightarrow {}^4T_1(F)$, $^4T_1(P)$.**—The assignment of these bands has been given earlier. At 4°K the number of fine components in the $^4T_1$(F and $^4T_1$(P) bands, Figure 3, Table I, is larger than that which can be accounted for by spin–orbit coupling alone and undoubtedly represents a combination of spin–orbit origins, low-symmetry components, and vibrations. More cannot be said owing to a lack of definitive polarization data.

**Acknowledgment.** This research was supported in part by NSF Grant GP-7920.

---

(13) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 346.

(15) Based upon: *Dq*(Td $Co^{2+}$ in garnet) ≈ 460 $cm^{-1}$,[12] with the oxygen charge being about twice that of fluorine, or *Dq*(Td for $F^-$ as a ligand) ≈ 300 $cm^{-1}$;[11] from the consideration that *Dq*(cubic) should equal ∼2*Dq*(Td), we would expect *Dq*(cubic) to be 460–600 $cm^{-1}$.

(16) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 70.

(17) J. D. Axe and G. D. Pettit, *J. Phys. Chem. Solids*, **27**, 621 (1966).

---

CONTRIBUTION FROM THE CENTER OF MATERIALS RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND 20742

# The Effect of High Pressure on the Vibrational Spectra of Square-Planar Coordination Compounds

By JAMES R. ALLKINS, ROBERT J. OBREMSKI, CHRIS W. BROWN, AND ELLIS R. LIPPINCOTT

*Received August 1, 1968*

The effect of high pressures (up to 50 kbars) on the molecular vibrations of square-planar coordination compounds of the type $MX_2L_2$ (where M = $Pt^{II}$ or $Pd^{II}$, X = Cl or Br, and L = $(CH_3)_2S$) has been studied over the infrared spectral frequency range, 4000–200 $cm^{-1}$. Emphasis has been placed on the region containing the molecular vibrations of the ligand and it is shown that certain molecular motions are more sensitive than others to changes in the external pressure, both in terms of frequency shifts and changes in intensity. Conclusions are reached as to the effectiveness of this technique for deducing vibrational assignments.

## Introduction

A recent report by Postmus, Nakamoto, and Ferraro[1] has described the effect of high pressure on the symmetric and antisymmetric metal–halogen stretching modes of four types of coordination compounds. Their results show that whereas the peak positions are relatively insensitive to pressure, the intensity of the symmetric metal–halogen stretching mode decreases markedly, compared to that of the antisymmetric mode, with increasing external pressure. It was concluded that this technique may be used in the assignment of metal–halogen and metal–ligand stretching vibrations in coordination compounds of suitable symmetry. From their study it would appear that the technique may prove valuable in the interpretation of absorptions in higher spectral regions. The vibrational assignment of the spectra of coordination compounds containing more than seven atoms is, at the very least, difficult. Thus, it was decided to extend the above study to include molecular vibrations of the ligand in the hope of elucidating the nature of this rather interesting effect.

---

(1) C. Postmus, K. Nakamoto, and J. R. Ferraro, *Inorg. Chem.*, **6**, 2194 (1967).