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Infrared absorption spectra of divalent cobalt ions in cadmium-chloride-type crystals*

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The polarized infrared absorption spectra of divalent cobalt ions at concentrations from 0.5 to 10 wt% in cadmium-chloride, cadmium-bromide, manganese-chloride, and cobalt-chloride crystals from 5 to 300°K are reported. The spectra comprise both magnetic-dipole-allowed electronic transitions and electric-dipole-allowed vibronic lines and bands. The electronic lines due to single cobalt ions are assigned to transitions between the spin-orbit and trigonal-crystal-field split levels of the ${}^4T_{1g}({}^4F)$ ground term. Their frequencies match those of lines in the electronic Raman spectra of the same crystals while their oscillator strengths are in quantitative agreement with those calculated using complete $3d^7$ configuration crystal-field theory. Electronic lines due to cobalt-ion pairs are also observed and are interpreted using the isotropic Heisenberg exchange interaction $-J(1/2+2\vec{S}_1\cdot\vec{S}_2)$. For the cadmium-chloride crystals, the exchange splitting of the ground level requires a J of $+5.0\pm0.1$ cm^{-1}, which predicts an additional level at 8.5 cm^{-1}. This has been observed at 8.55 cm^{-1} in the crystals by far-infrared absorption spectroscopy. The exchange splittings of the other spin-orbit levels are satisfactorily fitted using different values of J. The electronic lines observed in antiferromagnetically ordered cobalt chloride are also reported. The vibronic lines and bands observed correspond to peaks in the phonon density of states of the host crystals. A distinctive feature of these vibronic spectra are the very sharp low-frequency peaks at 73, 85, 90, and 60 cm^{-1} for cadmium, manganese, and cobalt chloride and cadmium bromide, respectively.

I. INTRODUCTION

The energy levels of the $3d^7$ configuration characterize the electronic spectra of divalent cobalt ions. In this paper, we describe and analyze the infrared absorption spectra of crystals of cadmium chloride, cadmium bromide, and manganese chloride containing cobalt and of cobalt chloride.

The infrared spectra comprise both pure electronic transitions between the energy levels of the ${}^4T_{1g}({}^4F)$ cubic-field term, and their vibronic bands. The pure electronic transitions are relatively weak and the vibronic bands are the principal spectral features.[1,2] This has lead to some incorrect analyses of cobalt infrared spectra in the past.

The Raman scattering spectra of the same crystals have been reported in an earlier paper[3] henceforth referred to as I. The Raman spectra yield the frequencies of all five pure electronic transitions of the ${}^4T_{1g}({}^4F)$ cubic-field term and so allows the identification of these transitions in the infrared absorption spectra.

Hsu and Stout[4] have reported the polarized infrared spectra of cobalt chloride crystals with results in agreement with ours. We suggest an assignment for some of their unassigned lines. The infrared spectra observed are described in Sec. III, and analyzed in Secs. IV–VI.

II. EXPERIMENTAL

All crystals were grown and prepared in the manner described in I. A Beckman IR12 infrared spectrophotometer was used to obtain the absorption spectra over the 200–4000-cm^{-1} range, at a wave-number accuracy of better than 0.5 cm^{-1}. Spectra appearing in the figures were traced directly from the spectrophotometer chart recordings.

Polarization spectra were recorded using either a Beckman silver chloride polarizer or Cambridge Model No. IG225 polarizer. These polarizers were located in the combined beam, after the monochromator. Increased slit widths were needed to compensate for the transmission loss in the polarizer resulting in the polarization spectra having less resolution than the axial spectra.

The crystals used for the axial spectra measurements were aligned such that the infrared radiation passed through the cleaved faces. For the polarization spectra, crystals with flat surfaces perpendicular to the cleaved faces were needed. These were obtained by grinding and polishing the samples in a dry box.

For crystal temperatures down to 15°K, the crystals were cooled in a Hofman conduction-type Dewar equipped with cesium bromide or cesium iodide windows. For low-temperature spectra below 15°K it was necessary to use an alternative Dewar in which the sample is cooled by liquid helium directed at it through a jet. This Dewar required two inner chamber windows that could withstand liquid-helium temperature. Cesium bromide windows mounted on copper flanges with Araldite were used.[5]

For the recording of low-temperature spectra on the Beckman spectrophotometer, the second chopper had to be stopped in order to prevent thermal-emission effects from producing a spurious spectral signal of zero transmission below 800 cm^{-1}.

III. DESCRIPTION OF THE SPECTRA

The axial and polarized spectra of cadmium chloride and cadmium bromide crystals containing 0.5%, 1.0%, 2.5%, 5.0%, 7.5%, and 10.0% by weight of cobalt were measured from 400 to 1500 cm^{-1}. For comparison, axial spectra were also recorded for cobalt chloride and crystals of manganese chloride containing 1.0-, 5.0-, and 10.0-wt% cobalt.

The room-temperature spectra of all the crystals are characterized by a broad band centered at approximately 1160 cm^{-1} in the chlorides and 1100 cm^{-1} in cadmium bromide. An additional band near 650 cm^{-1} appears at weak intensity in thick samples of the heavily cobalt-doped crystals. The intensity of both broad bands increases with temperature indicating their vibronic origin. At low temperatures a further broad band appears near 1260 cm^{-1} in the chlorides and 1170 cm^{-1} in cadmium bromide, while sharp lines occur on the low-frequency side of all three bands (Fig. 1).

The intensities of both bands and lines depends on the cobalt concentration and they are absent in both pure and nickel-doped crystals of cadmium chloride, cadmium bromide, and manganese chloride. Some of the lines have intensities that increase linearly with the cobalt concentration, while others have intensities that increase more rapidly and appear as additional lines in the more heavily doped crystals (Fig. 2). Some of the vibronic lines are absent from the lowest-temperature spectra.

The sharp lines are assigned as either pure-electronic no-phonon transitions of the cobalt ion or vibronic transitions associated with these electronic transitions.

The pure-electronic lines are identified by the coincidence of their frequencies, to within 1 cm^{-1}, of those of electronic transitions of cobalt observed in the electronic Raman spectra of the same crystals. These no-phonon lines form parents for the vibronic lines which are located symmetrically about them, with the lower-frequency component having a vanishing intensity at low temperature.

The electronic lines may be classified according to the dependence of their intensity on the cobalt ion concentration. Figure 2 shows the infrared spectra of cadmium chloride crystals containing cobalt for varying cobalt concentrations. The spectra of the crystals containing 0.5- and 1.0-wt% arise from cobalt ions located in the regular cation sites of the host crystals and having no neighboring cobalt ions. These low-concentration cobalt spectra constitute the single cobalt ion spectra which are discussed in Sec. IV.

As the cobalt ion concentration is increased the lines of the single cobalt ion spectra broaden and shift to lower frequencies. New lines appear with intensities which increase rapidly with the cobalt concentration to become comparable with those of the single ion spectra at a concentration of approximately 10 wt%. These new lines are, therefore, attributed to cobalt-ion clusters, where a cobalt ion in a cation site has one or more cobalt ions located in neighboring cation sites. The relative probability of occurrence of each kind of cobalt-ion cluster arrangement can be derived as follows:

The structure of cadmium-chloride-type crystals has been given by Ono *et al.*[6] Within each cation layer each ion has six nearest neighbors and, since each cation layer is separated by two anion layers, interlayer effects between cations can be

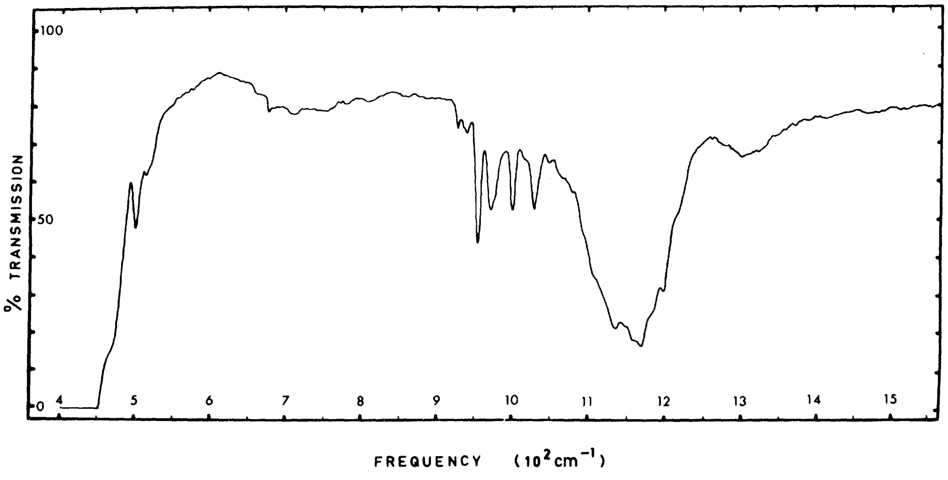

FIG. 1. Axial infrared absorption spectra of cadmium chloride crystals containing 7.5 wt% of cobalt chloride recorded at 15 °K.

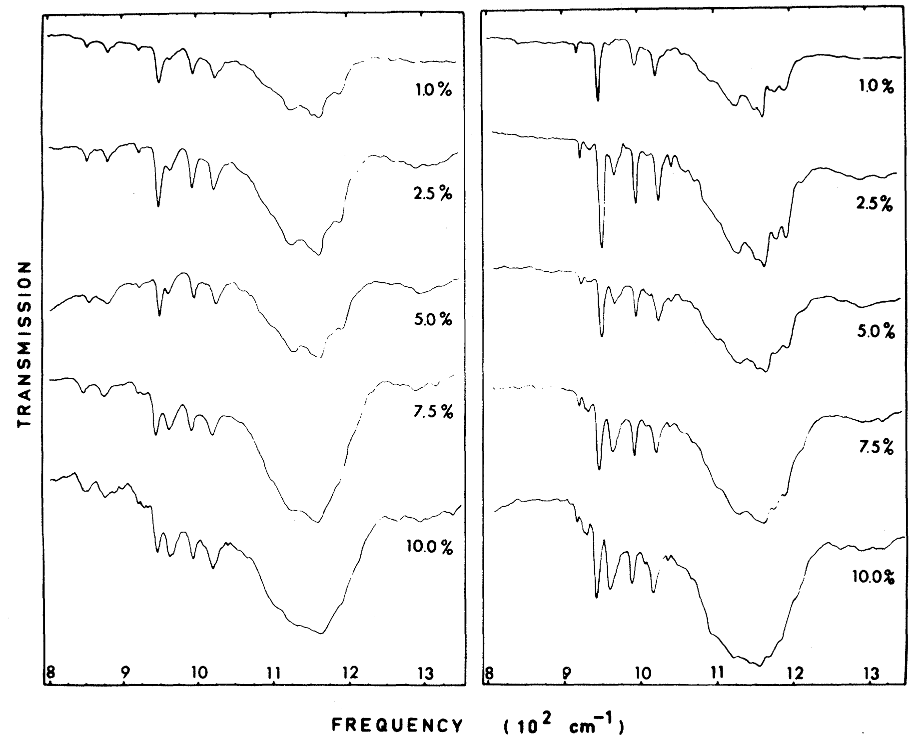

FIG. 2. Axial infrared absorption spectra of cadmium chloride crystals containing 1.0% (2.80 mm), 2.5% (3.33 mm), 5.0% (2.05 mm), 7.5% (1.82 mm), and 10.0% (1.33 mm) by weight of cobalt chloride. The spectra on the left-hand side were recorded at 78 °K and those on the right-hand side at 15 °K.

ignored. We assume a random distribution of cobalt ions in each and every cation layer and that there is no segregration of cobalt ions in any one region of the crystal. Let N be the total number of cations, c is the mole fraction of cobalt ions, and $1-c$ is the mole fraction of cadmium ions. For the number of single cobalt ions with concentration c all six nearest neighbors of a given cobalt ion site must be cadmium ions and the number is $Nc(1-c)^6$. The number of cobalt ion pairs is $6Nc^2(1-c)^8$.

From these numbers, the probability of their occurrence may be obtained by dividing by the number of sites N available. For crystals with a cobalt concentration of between 5 and 10 wt% the spectra will comprise lines due to single cobalt ions and cobalt-ion pairs. The spectra of the pairs are discussed in Sec. VI.

IV. SINGLE-ION COBALT SPECTRA

The pure electronic lines of single cobalt ions are identified by the linear dependence of their intensity on the cobalt-ion concentration. The lines observed in the infrared spectra below 2000 cm^{-1} are transitions between the spin-orbit and trigonal-crystal-field levels of the $^4T_{1g}(^4F)$ cubic-field term. This term is split by the spin-orbit interaction to give four levels whose wave functions transform as the Γ_6^+, Γ_7^+, and Γ_8^+ irreducible representations of the cubic double group. There are two levels transforming as the Γ_8^+ representation and these are distinguished as $^{(1)}\Gamma_8^+$ and $^{(2)}\Gamma_8^+$. The trigonal component of the crystal field shifts and splits these spin-orbit levels. The Γ_6^+ and Γ_7^+ levels transform as the γ_4^+ irreducible representation of the D_{3d} trigonal double group, while the Γ_8^+ levels are split by the trigonal crystal field into states transforming as the γ_4^+ and $\gamma_{5,6}^+$ irreducible representations. Here $\gamma_{5,6}^+$ denotes the complex-conjugate pair $(\gamma_5^+ + \gamma_6^+)$ which is degenerate in zero magnetic field.

Of the five electronic transitions identified by Raman scattering in I, only three are observed in the infrared spectra (Table I). The transition to the lowest-energy electronic level $|^{(1)}\Gamma_8^+, \gamma_{5,6}^+\rangle$ was not observed because it lies in the region of reststrahlen absorption of the host crystal, while the transition to the uppermost level $|\Gamma_7^+, \gamma_4^+\rangle$ of the $^4T_{1g}(^4F)$ term was not observed because of its weak intensity (Table II) together with its masking by the broad absorption band near 1170 cm^{-1} in the chlorides.

For all three lines, identified as purely electronic by comparison with the Raman-scattering spectra, the axial and π polarization spectra coincide showing that the electronic transitions are magnetic dipole allowed (Fig. 3).

The transitions are from a $|\Gamma_6^+, \gamma_4^+\rangle$ ground state to excited states of either γ_4^+ or $\gamma_{5,6}^+$ symmetry and

TABLE I. Observed frequencies (cm^{-1}) and widths (cm^{-1}) of single-cobalt-ion electronic transitions recorded for crystals of $CdCl_2:Co^{2+}$, $CdBr_2:Co^{2+}$, $MnCl_2:Co^{2+}$ at 15 °K and $CoCl_2$ at 30 °K.

Assignment	$CdCl_2$:0.5-wt% Co Freq. (cm^{-1})	 Width (cm^{-1})	$CdBr_2$:1.0-wt% Co Freq. (cm^{-1})	 Width (cm^{-1})	$MnCl_2$:1-wt% Co Freq. (cm^{-1})	 Width (cm^{-1})	$CoCl_2$ Freq. (cm^{-1})	 Width (cm^{-1})
$^{(1)}\Gamma_8^+\gamma_4^+$	498.5 ± 0.5	5	...		...		545 ± 1	25
$^{(2)}\Gamma_8^+\gamma_4^+$	922.3 ± 0.4	2	887 ± 1	1	939 ± 1	8	962 ± 1	20
$^{(2)}\Gamma_8^+\gamma_{5,6}^+$	951.1 ± 0.3	3	893.1 ± 0.3	1	972 ± 1	12	993 ± 1	

have different polarization selection rules depending on the excited state of the transition. The magnetic dipole transition operator M_i is

$$M_i = (1/6mc)(L_i + 2S_i) \quad (i = x, y, z),$$

where L_i and S_i are the components of the orbital and spin angular momentum, respectively, and m is the electronic mass. Its components M_z and M_x transform as the γ_2^+ and γ_3^+ irreducible representations of the D_{3d} double group. From the product representations

$$\gamma_4^+ \times \gamma_2^+ \rightarrow \gamma_4^+, \quad \gamma_4^+ \times \gamma_3^+ \rightarrow \gamma_4^+ + \gamma_{5,6}^+,$$

it follows only γ_4^+ electronic upper states can be observed in the σ polarization spectra. This yields the assignment of the three observed electronic lines given in Table I.

The crystal-field calculation of I yields single-ion wave functions which may be used to calculate the intensities of these magnetic dipole transitions. The oscillator strength f of a magnetic dipole transition between two states $|g\rangle$ and $|e\rangle$ is given by

$$f = (4\pi m\nu/h)\,|\langle g|M_i|e\rangle|^2,$$

where ν is the frequency of the transition and M_i is the magnetic-dipole transition operator.

The oscillator strengths were determined experimentally from the peak absorbance and half-width of each infrared absorption line using the formula of Dexter.[7] The absorption data for cadmium chloride and cadmium bromide crystals containing 0.5 and 1.0 wt% of cobalt were used, together with data for the 10-wt% crystals where necessary. The refractive index of cadmium chloride in the visible is 1.68 while its value in the infrared was estimated from the measured transmittances of 0.78 ± 0.02 and 0.80 ± 0.02 at 1500 and 900 cm^{-1}, respectively. With an allowance of 5% for surface scattering by the crystal faces, a value of 1.84 was calculated. For cobalt chloride, Hsu and Stout obtained a value of 1.87.

The number of absorbing ions per unit volume was calculated from the crystal's molar doping and mean density. The accuracy of the doping of the crystals was checked by spectrophotometric measurements of a solution containing a known weight of the doped crystal and found to be accurate to within 2%.

With assumption of Gaussian lines, the experimental oscillator strengths are listed in Table II together with their calculated values. If other line shapes are assumed, the experimental values are

TABLE II. Calculated and experimental oscillator strengths for assigned transitions in $CdCl_2$:0.5-wt% Co and $CdBr_2$:1-wt% Co at 15 °K in units of 10^{-10}.

	$CdCl_2$:0.5-wt% Co				$CdBr_2$:1-wt% Co			
	Oscillator strength (σ)		Oscillator strength (π)		Oscillator strength (σ)		Oscillator strength (π)	
Assignment	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
$\gamma_4^+(\Gamma_6^+)$								
$\gamma_5^+ + \gamma_6^+(^{(1)}\Gamma_8^+)$		0		2868		0		3396
$\gamma_4^+(^{(1)}\Gamma_8^+)$	1103 [a]	5656	206 [a]	958.3		5285		1041
$\gamma_4^+(^{(2)}\Gamma_8^+)$	22.4	73.2	15.6	55.7	10.0	10.0	7.0	3.37
$\gamma_5^+ + \gamma_6^+(^{(2)}\Gamma_8^+)$	0	0	850	936.2	0	0	262	232.6
$\gamma_4^+(\Gamma_7^+)$		46.7		31.1		16.9		6.53

[a] $CdCl_2$:10-wt% Co at 78 °K.

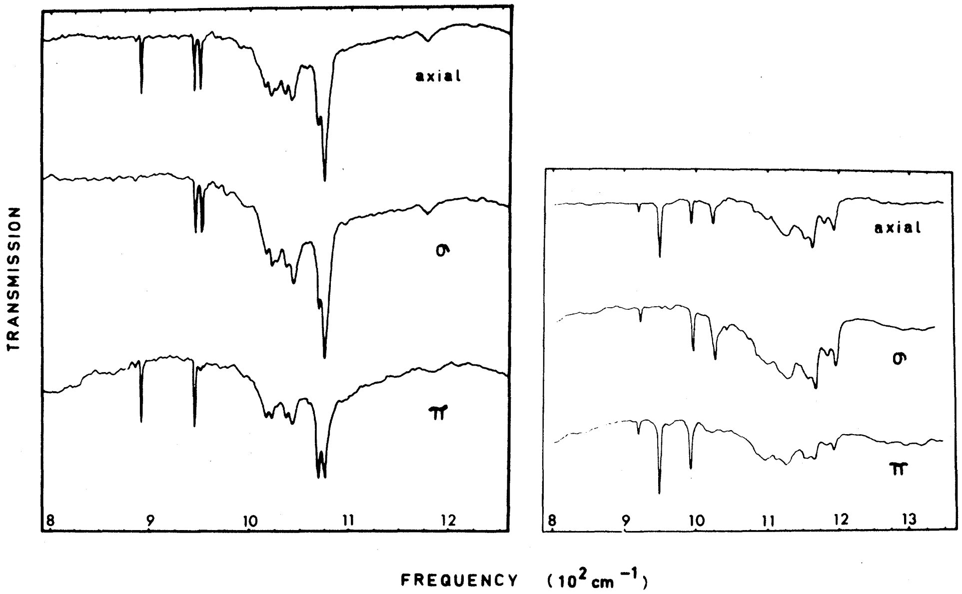

FIG. 3. Polarized infrared absorption spectra of cadmium bromide crystals containing 1.0 wt% of cobalt bromide (left-hand side) and cadmium chloride crystals containing 0.5 wt% of cobalt chloride.

modified, but in all cases the calculated values are sufficiently close to the experimental ones to support the assignment of the electronic lines as magnetic-dipole transitions between levels of the $^4T_{1g}(^4F)$ term.

V. SINGLE-COBALT-ION VIBRONIC SPECTRA

The vibronic spectra comprise both sharp lines and broad bands, neither of which are observed in the Raman spectra of the same crystals.

A. Sharp lines

The frequencies of the sharp vibronics are listed in Table III together with those of their no-phonon electronic parent transistions. They are assigned as vibronic in origin because they occur in pairs associated with a given electronic level and are located symmetrically about it. The lines are almost as narrow as their electronic parents and occur at a well defined vibronic interval for each crystal host, as can be seen in Table III.

The intensity of the lines is temperature dependent. The intensity of the summation line is proportional to $(1+n)$, while that of the difference line is proportional to n, where

$$n=[\exp(\hbar\omega/kT)-1]^{-1}. \tag{5.1}$$

Hence, the difference bands disappear at low temperature and are absent from the liquid-helium spectra for all crystals (Fig. 2). From the relative intensities of the summation and difference lines, the crystal temperature could be estimated. (The temperature of the 30 °K spectra recorded for $\mathrm{CoCl_2}$ and listed in Table I were obtained in this way.)

For polarized spectra the axial and σ-polarization spectra coincide indicating that the vibronic lines are electric-dipole allowed. The intensity of the vibronics follow that of their electronic parents but in the opposite polarization due to their electric rather than magnetic, dipole character.

Preliminary measurements of the spectra of cadmium bromide crystals containing divalent iron suggest that the vibronic intervals are characteristic of the crystal host rather than of one particular transition metal ion present.

The results for cobalt chloride are now discussed in more detail because of their relevance to the assignment of this crystal's spectra by Hsu and Stout.[4] First there is no evidence of the uniform 7-cm^{-1} discrepancy between the Raman and infrared data for $\mathrm{CoCl_2}$ reported by them. This apparent difference may be due to different crystal temperatures for the Raman and infrared measurements and the use of different crystals in separate laboratories. Sharp vibronic lines are observed by us for 905 and 1055 cm^{-1} at 78 °K. They are much broader than those observed in the other crystals and correspond to the unidentified vibronic lines at 900 and 1050 cm^{-1} reported by Hsu and Stout. By comparison with the data for the other isomorphic crystals they are assigned as difference and summation vibronic lines associated with

TABLE III. Frequencies (cm^{-1}) of the electronic-parent lines, the vibronics, and the vibronic intervals associated with the sharp acoustic phonon peaks observed in $CoCl_2$ and crystals of $CdCl_2$, $CdBr_2$, and $MnCl_2$ containing Co^{2+} ions.

Temp. (°K)	$CdCl_2$:1-wt% Co			$CdBr_2$:1.0-wt% Co			$MnCl_2$:1.0-wt% Co			$CoCl_2$		
	Electronic parent	Vibronic	Vibronic interval	Electronic parent	Vibronic	Vibronic interval	Electronic parent	Vibronic	Vibronic interval	Electronic parent	Vibronic	Vibronic interval
78	925 ±1	854 ±1	−71 ±2	. . .	832 ±1		940 ± 2	855 ± 2	−85 ± 4	963 ±4 [a]	1055 ± 2	+ 92 ± 6
		998.0 ± 0.7	+ 73 ±1.7		950.5 ± 0.6			1025 ± 2	+ 85 ± 4			
	953.2 ± 0.5	883 ±1	−70 ±1.5	896.5 ± 0.5	837 ±1	−59.5 ±1.5	975 ± 1	890 ± 2	−85 ± 3	994 ±1	905 ± 1	−89 ± 2
		1027.7 ± 0.8	+ 74.5 ± 1.3		956.5 ± 0.6	+ 59.7 ± 1.1		1062 ± 2	+ 87 ± 3		. . . [b]	
15	921.8 ± 0.4	995.1 ± 0.5	+ 73.3 ± 0.5	887 ±1	947.0 ± 0	+ 60 ±1.3	939 ± 1	1023 ± 1	+ 84 ± 2	960.0 ± 0.7	1051 ± 2	+ 91 ± 2.7
	950.2 ± 0.4	1025.0 ± 0.5	+ 74.8 ± 0.9	893.1 ± 0.3	953.2 ± 0.3	+ 59.9 ± 0.6	972 ± 1	1058 ± 1	+ 86 ± 2	981 ±2	1067 ± 2	+ 86 ± 4
										1012 ±1	. . . [b]	

[a] From Raman data, as not observed in infrared.

[b] Masked by lattice-phonon sideband.

the unresolved pair of electronic lines at 994 cm^{-1}. At 30 °K, the electronic parent line is resolved into two components at 962 and 993 cm^{-1} which agree to within 1 cm^{-1} of the Raman data for the same crystal (Table III of I). At 15 °K, the crystal is antiferromagnetically ordered with summation lines at 1051 and 1067 cm^{-1} associated with the 960- and 981-cm^{-1} parent lines. The expected summation line associated with the 1012-cm^{-1} line is masked by the broad vibronic band centered at 1220 cm^{-1}.

These summation lines yield a vibrational interval of 90 cm^{-1} for cobalt chloride, in comparison with 73 cm^{-1} for $CdCl_2:Co^{2+}$, 60 cm^{-1} for $CdBr_2:Co^{2+}$, and 85 cm^{-1} for $MnCl_2:Co^{2+}$. The low-frequency interval thus obtained is assigned to a sharp peak in the phonon density of states of the host crystals. It does not correspond in frequency to any of the known $\vec{k}=0$ phonons listed in Table IV which is consistent with the absence of any absorption at or near 73 cm^{-1} in the far-infrared spectra of cadmium chloride crystals.

It is expected that these sharp vibronic lines should also appear in the optical spectra of these crystals. In particular, it is suggested that the line at 18 887 cm^{-1} in the $^2T_2(^2P)$ term of $CdCl_2:Co^{2+}$ which is assigned by Mooney *et al.*[9] as a γ_4^+ symmetry electronic line could be vibronic in origin and associated with the other γ_4^+ symmetry line at 18 820 cm^{-1}. This is supported by the behavior of their spectra with temperature.

B. Broad bands

Broad vibronics bands associated with the same electronic parent lines are also observed. The bands are all electric-dipole allowed and have structure which was analyzed to give the frequencies of peaks in the phonon density of states for the host crystals (Table IV). In the case of the strongest band centered near 1170 cm^{-1} in the chlorides there are two parent electronic levels and hence all band peaks due to a given feature in the phonon density of states occur in pairs with a separation matching that of the $|^{(2)}\Gamma_8^+, \gamma_4^+\rangle$ and $|^{(2)}\Gamma_8^+, \gamma_{5,6}^+\rangle$ levels. These pairs of peaks show differing polarizations consistent with the different symmetries of their parents and this served to resolve ambiguities in their assignments (Fig. 3). The other broad bands are much weaker and show little structure. However, the observed peaks are consistent with those obtained for the strongest band. In particular, analysis of the highest-frequency band allowed the position of the electronic $|\Gamma_7^+, \gamma_4^+\rangle$ level to be inferred which confirmed the Raman results.

TABLE IV. Analysis of vibronic bands in $CdCl_2$:1-wt% Co and $CdBr_2$:1-wt% Co to give frequencies (cm^{-1}) of peaks in the phonon density of states at 15 °K.

	$CdCl_2$:1-wt% Co			$CdBr_2$:1-wt% Co	
Electronic parent	Vibronic	Vibronic interval	Electronic parent	Vibronic	Vibronic interval
921.8 ± 0.4	1100 ± 1	178.2 ± 1.5	887 ± 1	1017.5 ± 0.5	130.5 ± 1.5
	1128 ± 1	206.2 ± 1.5		1023.0 ± 0.5	136 ± 1.5
	1155 ± 1	233.2 ± 1.5		1038.2 ± 0.6	151.2 ± 1.6
	1164.5 ± 0.5	242.7 ± 1.0		1070.3 ± 0.5	183.3 ± 1.5
950.2 ± 0.4	1128 ± 1	177.8 ± 1.5	893.1 ± 0.3	1023.0 ± 0.5	129.9 ± 0.8
	1155 ± 1	204.8 ± 1.5		1029 ± 1	135.9 ± 1.3
	1183 ± 1	232.8 ± 1.5		1044.5 ± 0.5	151.4 ± 0.8
	1195 ± 1	244.8 ± 1.5		1076.5 ± 0.4	183.4 ± 0.7
1088 ± 3[a]	1265 ± 1	177 ± 5	995 ± 1[a]	1177 ± 2	182 ± 3
	1295 ± 2	207 ± 5			
	1320 ± 3[b]	232 ± 6			

$k=0$ phonons[c]				$k=0$ phonons[c]			
A_{1g}	E_g	A_{2u}	E_u	A_{1g}	E_g	A_{2u}	E_u
233 ± 1	131 ± 1	164 ± 2	210 ± 2	148 ± 1	77 ± 1	102 ± 2	161 ± 2

[a] Inferred from Raman results (Table IV of I)

[b] Weak, observed in 2.5-wt% and more heavily doped samples.

[c] D. J. Lockwood (Ref. 8).

VI. COBALT-ION PAIR SPECTRA

The most clearly resolved cobalt-ion pair spectra were observed using crystals containing 5-wt% cobalt and the spectra of these crystals were examined in detail.

The spectra observed for cadmium-chloride crystals are depicted in Fig. 4. The cobalt-ion pair absorptions form distinct groups, each being associated with a corresponding cobalt single-ion absorption. Each group is approximately 15 cm^{-1} higher in energy than the single-ion absorption due to the energy level splitting of the ground state of the cobalt-ion pair. The frequencies of the electronic pair lines are shown on the energy level scheme in Fig. 5 while the associated vibronic lines all have a common interval of 73 cm^{-1} from their electronic parents. The energy level at 34 cm^{-1} was inferred by the observation of pair lines at 903 and 930 cm^{-1}, which are absent from the lowest-temperature (5 °K) spectra.

To obtain the frequencies of the pair lines in the 0–50-cm^{-1} spectral region, the far-infrared absorption spectra of the cadmium chloride crystals were measured by Campbell[10] while at Cornell University. These did not show a transition at 34 cm^{-1}, but revealed a strong line at 8.55 cm^{-1} with a $g_{\parallel}$ factor twice that of the single cobalt ion $|\Gamma_6^+, \gamma_4^+\rangle$ ground state. This line is, therefore, assigned as an energy level of the cobalt-ion pair.

The spectrum of cadmium bromide crystals con-

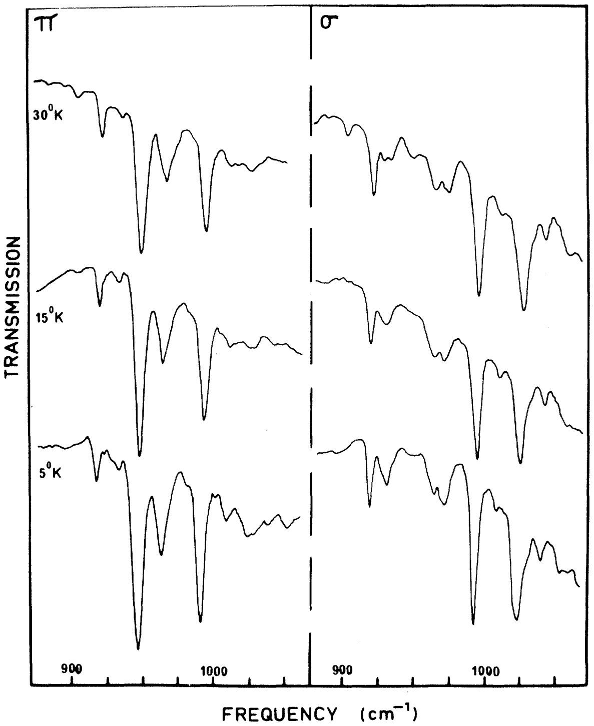

FIG. 4. Polarized infrared absorption spectra of cadmium chloride crystals containing 5 wt% of cobalt chloride recorded at 30, 15, and 5 °K between 875 and 1075 cm^{-1}. The π-polarization spectra are on the left-hand side and the σ-polarization spectra on the right-hand side.

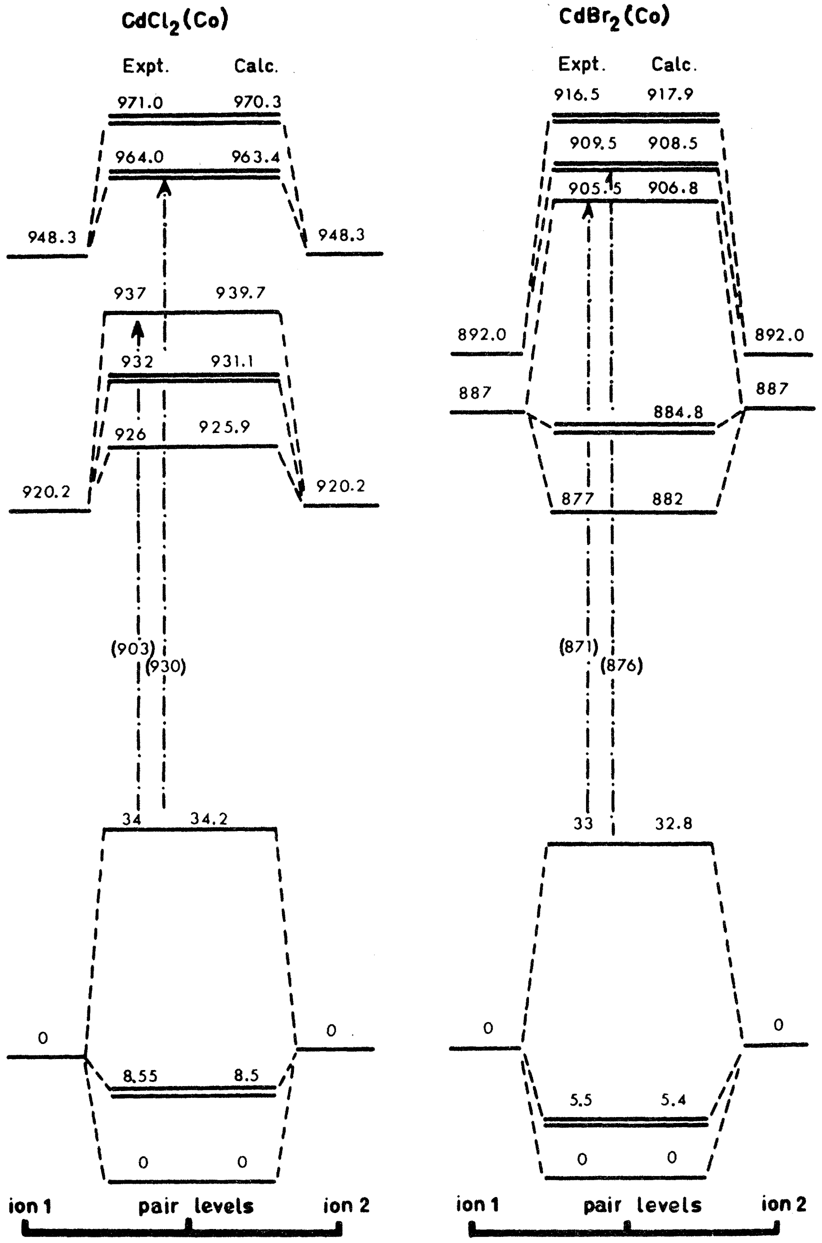

FIG. 5. Calculated and observed energy levels for exchange-coupled cobalt-ion pairs in cadmium chloride and bromide crystals containing 5 wt% of cobalt. The chloride spectrum is on the left-hand side.

taining 5 wt% of cobalt are shown in Fig. 6. All the absorption lines are narrower and weaker than those in cadmium chloride, and the spectra are more complex with some superimposed lines. The frequencies of the electronic lines are shown in Fig. 6, while their associated vibronic lines have a common 60-cm^{-1} separation from their electronic parents. An additional line at 928 cm^{-1} has an intensity which increases faster than quadratically with the cobalt concentration and this line is assigned to a higher-order cobalt cluster. The energy level at 33 cm^{-1} is inferred from the lines at 871 and 876 cm^{-1}, which disappear at low temperatures.

Preliminary far-infrared measurements[10] on a 10-wt% cadmium bromide crystal reveal an absorption at 6.2 cm^{-1}, which appears to be an analog of the level at 8.55 cm^{-1} observed in the chloride. The presence of such a level has been postulated by Bailey *et al.*[11] who obtained a frequency of 5.5 cm^{-1} from the optical spectra of the crystals. Zeeman studies are needed to confirm that the 6.2-cm^{-1} line in the far infrared due to cobalt-ion pairs and the frequency of 5.5 cm^{-1} obtained by

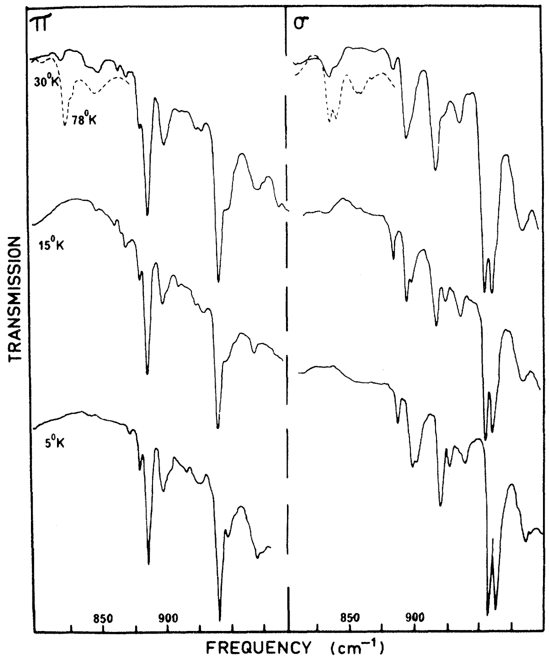

FIG. 6. Polarized infrared absorption spectra of cadmium bromide crystals containing 5 wt% of cobalt bromide recorded at 78, 30, 15, and 5 °K between 800 and 1000 cm^{-1}. The π-polarization spectra are on the left-hand side and the σ-polarization spectra on the right-hand side.

Bailey is used in our exchange-splitting fittings.

The model used for the interpretation of the cobalt-pair spectra is that of exchange-coupled cobalt-ion pairs. The Hamiltonian of the pair system is

$$\mathcal{H} = \mathcal{H}_0(1) + \mathcal{H}_0(2) + \mathcal{H}_{12},$$

where $\mathcal{H}_0(1)$ and $\mathcal{H}_0(2)$ are the crystal-field Hamiltonians of the two cobalt ions 1 and 2, respectively, and $\mathcal{H}_{12}$ is the isotropic Heisenberg exchange interaction

$$-J(\tfrac{1}{2} + 2\vec{S}_1 \cdot \vec{S}_2),$$

where J is the exchange-interaction parameter, and S_1 and S_2 are the spins of the two cobalt ions. The zero-order states of the pair system are the product states $|\psi_1\rangle|\psi_2\rangle$, where $|\psi_1\rangle$ and $|\psi_2\rangle$ are the wave functions of the two single ions 1 and 2 given by the crystal-field analysis in I.

As all the observed electronic transitions are between energy levels of the ${}^4T_{1g}({}^4F)$ terms there are 144 possible pair-product states that can be formed from the 12 single-ion states of each ion. Since either ion may be excited in a pair the pair states have a degeneracy which is lifted by off-diagonal energy transfer processes that transfer the excitation from one ion to the other. These energy-transfer-induced splittings are much smaller than the direct exchange splittings of a pair state. This is shown by the relative magnitudes of the product state $|\psi_1\rangle|\psi_2\rangle$ matrix elements

$$\langle\psi_1|\langle\psi_2|\vec{S}_1\cdot\vec{S}_2|\psi_2\rangle|\psi_1\rangle \quad \text{and} \quad \langle\psi_1|\langle\psi_2|\vec{S}_1\cdot\vec{S}_2|\psi_1\rangle|\psi_2\rangle,$$

respectively. For the energy levels at 948.3 and 920.2 cm^{-1} observed in the single-ion spectra the off-diagonal matrix elements have magnitudes typically $\frac{1}{50}$ of the diagonal elements. Hence we may with little error restrict our pair states to the 24 product states in which only ion 1 is excited and ion 2 remains in its ground state. The matrix elements of the operators $\vec{S}_1 \cdot \vec{S}_2 = S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z}$ are evaluated between these 24 states, using the S_x and S_z matrix elements of I. The matrix elements of $S_{1y}S_{2y}$ are of the same magnitude but may have differing signs from those of $S_{1x}S_{2x}$, so the matrix elements of $S_{1x}S_{2x} + S_{1y}S_{1y}$ are either twice those of $S_{1x}S_{2x}$ or zero.

The resulting energy matrix is diagonalized to give the exchange-coupled cobalt-ion pair energy-level scheme as a function of the exchange interaction parameter J. The different orbital character of the various single-ion levels Γ^+ of the cobalt ion within the ${}^4T_{1g}({}^4F)$ term required different values of J for each Γ^+ multiplet. The crystal-field energies of the single cobalt ion in the low-symmetry site of a pair are also required for $\mathcal{H}_0(1)$ and these differ by a few cm^{-1} from the values for an isolated single cobalt ion in the regular cation site, and comprise the single-ion energy-level shifts.

The experimental data for cadmium chloride in Fig. 5 was fitted using a separate exchange parameter J for each Γ^+ multiplet and allowing for the pair-induced shift in the single-ion levels. For cadmium chloride, the ground-state splitting is fitted with a J of $+5.0 \pm 0.1$ cm^{-1}, while the excited states are fitted with a J of magnitude 2.6 ± 0.3 cm^{-1} together with single-ion energy-level shifts of +4.0 and −2.0 cm^{-1} for the 948.3- and 920.2-cm^{-1} states, respectively. The sign of the exchange parameter for the ground state indicates that the exchange interaction between these states is ferromagnetic. The sign of J for the excited states cannot be determined without additional data such as that provided by Zeeman studies.

As a check on the validity of the approximation of neglecting the off-diagonal energy-transfer matrix elements, the energy matrix with all the 144 product states was also constructed and diagonalized for the particular J values given above. The eigenvalues of this matrix differ from those of the dimension-24 matrix by, at most, 0.2 cm^{-1}, which justifies the use of the truncated (dimension-24) energy matrix for the J parameter fittings.

For cadmium bromide, the analysis was less straightforward because the single-ion levels at 887 and 892 cm^{-1} are relatively close. For the ground state, a $J=+5.2\pm0.1$ cm^{-1} was obtained which corresponds to ferromagnetic exchange. The two excited states could only be fitted with J's of equal magnitude 5.3 ± 0.3 cm^{-1} but of opposite sign for the two levels, being negative for the 887-cm^{-1} level and positive for the 892-cm^{-1} level. The corresponding single-ion energy-level shifts are -3.0 and $+0.5$ cm^{-1}, respectively.

As can be seen from Fig. 5, the model is successful in reproducing the observed level-splitting patterns for both cadmium chloride and cadmium bromide using a minimum number of parameters. For cadmium chloride the level at 34 cm^{-1} was fitted exactly by adjusting the ground-state isotropic exchange parameter which also gave the position of the 8.5 cm^{-1} level prior to the far-infrared measurements at Cornell. Similarly, a level was predicted at 5.4 cm^{-1} for the bromide, in close agreement to Bailey's value of 5.5 cm^{-1}. The fitting of the excited states is also very good, especially for the chloride. However, Zeeman measurements would be helpful to fix the sign of J for the excited states and check the assignments.

One advantage of the model is that it uses a purely isotropic exchange interaction. There is no need to introduce any additional anisotropic exchange parameters to fit the spectrum, as would be the case if the levels were characterized by an effective or pseudospin of $S'=\frac{1}{2}$ or $\frac{3}{2}$. In particular if the ground-state-splitting pattern is to be fitted using an effective spin $S'=\frac{1}{2}$ for each ion, it is necessary to use an anisotropic exchange spin Hamiltonian of the form

$$\mathcal{H}_{12}=-2J_{\parallel}S_{1z}S_{2z}-2J_{\perp}(S_{1x}S_{2x}+S_{1y}S_{2y}),$$

with the parameter values $J_{\parallel}=+8.5$ and $J_{\perp}=17.0$ cm^{-1}.

The spin-Hamiltonian formalism has been applied with some success to the optical spectra of cobalt in cadmium bromide crystals by Bailey *et al.*[11] It would be useful to reinterpret their data using an isotropic exchange interaction for the wave functions determined by the complete crystal-field analysis done in I. However, attempts to do such a reinterpretation were unsuccessful due to the inability to obtain any crystal-field splittings of any Γ_8^+ quartets in the 17 700-cm^{-1} region that would match the 6-cm^{-1} separation of the single ion levels reported by Bailey, using the values of trigonal-field parameters v and v' of I. The values of v and v' would have to be reduced to 20% of their values or their ratio considerably altered to achieve any fit. A Ham-effect reduction would be needed to justify any such changes and it would not then be appropriate to use the wave functions obtained with reduced v and v' parameters. Clearly, further work on the crystal-field analysis of the single-ion spectra is needed before one can usefully attempt the interpretation of the Bailey *et al.* results on an isotropic exchange model.

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