Luminescence from the $^2T_{2g}(H)$ State of Cobalt(II)-Doped $KCdBr_3$

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Using argon-ion laser excitation, luminescence has been observed at low-temperature (14 K) in the region between 17 500 and 20 000 cm^{-1}, for single crystals of cobalt(II)-doped $KCdBr_3$. This luminescence is assigned to transitions from the lowest energy component of the $^2T_{2g}(H)$ state, $^2A''$ in the C_s point symmetry of the cobalt(II) site, into the $^4T_{1g}(F)$ ground state manifold. It gives rise to two broad bands with sharp origins at 20029 and 19127 cm^{-1} upon which is superimposed considerable vibronic structure. This is believed to be the first example of luminescence detected from the $^2T_{2g}(H)$ state of the cobalt(II) ion. However, as the intensity drops markedly between 14 and 70 K, this transition is not a suitable candidate for the investigation of laser action. Electronic Raman transitions to excited state components of the ground state have been observed, though these are a factor of 50−100 times weaker than the luminescence band origin at 20 029 cm^{-1}. The energies of the observed electronic Raman transitions were found to correlate with sharp vibronic components of the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ transition, which confirmed the ground state spinor component energies to be 262, 500, 902, 1052, and 1118 cm^{-1}. Finally, the quenching of background emission intensity is indicated by the appearance of "holes" in the observed spectra which are due to absorption into various electronic states of the cobalt(II) ion. This emphasises the importance of crystal quality, the presence of other impurities, and even the role of the host material in determining the optical properties of crystals.

Introduction

Luminescence from systems involving cobalt(II) ions is comparatively unusual. Many previous studies noting this behavior describe doped semiconductors[1−25] or are relatively recent,[26−42] a consequence of renewed interest in solid state materials for the development of tunable laser systems.[43−66] Although room-temperature infrared laser action had been demonstrated in the mid 1960's,[67,68] much recent interest has

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centered upon the material, Co^{2+}-doped MgF_2, in the region 1.75−2.5 μm.[69-90] After several years of development, a flashlamp pumped laser based upon this material is now being used in both medical and dental applications, and improved eye safety for midinfrared wavelengths makes it a candidate for light detection and ranging (LIDAR) sources and remote sensing instruments designed to operate spacecraft or aircraft.[87] CW infrared laser action has also been demonstrated for Co^{2+}-doped $KZnF_3$,[26,88,91] while Co^{2+}-doped ZnF_2[67,92] and $KMgF_3$[67,88] have been shown to be potential laser materials.

Normally the parent emitting state of a six coordinate cobalt(II) ion is the lowest energy one, $^4T_{2g}$, since nonradiative energy transfer mechanisms are often too efficient to allow emission to be observed from higher energy states. However, although the observation of luminescence involving electronic states which are not the closest in energy to the ground state is unusual, it has been noted for Co^{2+} ions in various tetrahedral sites.[27,35,40-42,93] In contrast, the Ni^{2+} ion doped into a variety of crystals for which the site symmetry is six coordinate exhibits a number of metastable emitting states.[94-100] The authors now wish to describe luminescence involving the cobalt(II) ion in a six coordinate site which arises from the $^2T_{2g}(H)$ state of Co^{2+}-doped $KCdBr_3$ single crystals.

Experimental Section

Crystals of cobalt(II)-doped $KCdBr_3$ were produced using KBr, $CdBr_2{\cdot}4H_2O$, and $CoBr_2{\cdot}nH_2O$ as starting materials. Initially, a 1:1 saturated solution of KBr and $CdBr_2{\cdot}4H_2O$ was heated to remove most of the water and dried overnight at 120 °C. The resultant powder was melted under vacuum in a silica tube to remove residual water, producing crystals of $KCdBr_3$. These crystals were ground, a ~3% molar ratio of anhydrous $CoBr_2$ was added, and the mixture was sealed in silica ampules under vacuum. Crystals of the doped material were grown in a Bridgman furnace at 750−800 °C and, after removal from the cooled ampules, stored in a desiccator.

The crystal structure of $KCdBr_3$ belongs to the same space group as $KCdCl_3$, D_{2h}^{16} (*Pnma*) ($Z = 4$).[101,102] This has been verified by X-ray powder studies,[101] Raman spectroscopy,[103] and absorption spectroscopy.[104] The *c* crystal axis was identified by poor crystal cleavage in this direction, and with the aid of a polarizing microscope, the crystal faces were determined and polished with the polarization directions parallel to the edges. In the $KCdX_3$ (X = Cl and Br) systems, the Cd^{2+} ion site symmetry is rigorously C_s. Similarly, the point symmetry of a

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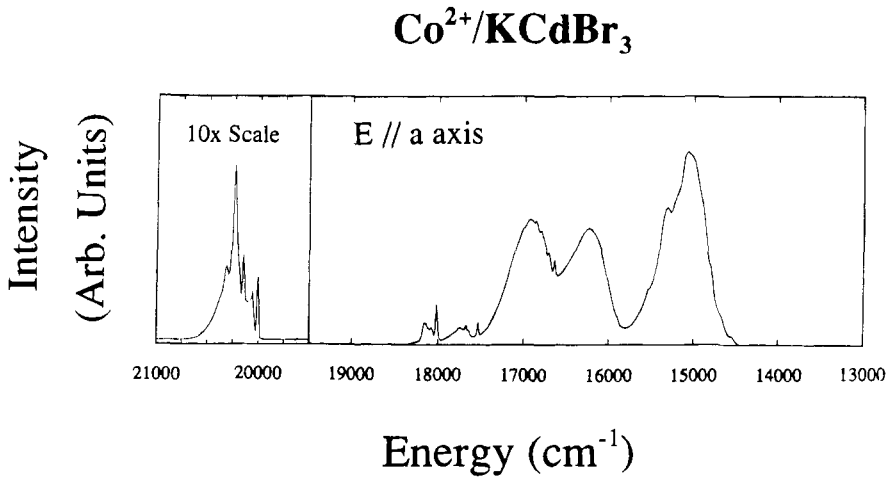

Figure 1. Low-temperature (14 K) *a*-polarized absorption spectrum for 2% Co^{2+}-doped $KCdBr_3$.[104] The region containing the $^4A''(^4T_{1g}(F)) \rightarrow {}^2T_{2g}(H)$ transitions has been expanded for clarity.

dopant Co^{2+} ion is C_s, as it has been shown that the polarization properties of the electronic transitions cannot be accounted for in a point group of higher symmetry.[104]

The Raman and luminescence spectra were measured using a Cary 81 spectrophotometer fitted with an S20 photocathode and either the 488.0, 476.5, or 457.9 nm lines of a Spectra-Physics 2020 argon-ion laser excitation source with typical output power of 100 mW. Single crystals of $Co^{2+}/KCdBr_3$ were mounted on a copper block attached to a cold head and cooled by a Displex closed cycle-refrigeration system to a temperature no lower than 14 K. The Raman and luminescence spectra were obtained up to 70 K using a Displex temperature controller and monitored by a Thor cryogenics sensor. Polarized luminescence was obtained by inserting a polarizer and then a polarization scrambler between the sample and the detector. For the purposes of the following discussion of the measured spectra, the energy units are in cm^{-1}, the energy of the laser excitation being denoted by ν_{ex} and the energy of the detected radiation by ν. The intensities were not corrected for the wavelength response of the monochromator and photomultiplier and hence cannot be compared when different excitation lines of the argon-ion laser have been used.

Results and Discussion

Luminescence in Cobalt(II)-Doped Systems. Luminescence due to the cobalt(II) ion in six coordinate oxide and halide crystals is normally observed in the region of the $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ transition, between 5000 and 7000 cm^{-1}.[26-42,56,67,91,92,106,107] Ralph and Townsend[106] reported near-infrared fluorescence for the Co^{2+}/MgO system commencing at 8150 cm^{-1}, assigning transitions from both the $^4T_{2g}$ and ^2E_g states. Sturge[107] has observed broad infrared luminescence for the Co^{2+}-doped $KMgF_3$ system and has identified sharp zero-phonon lines due to the $^4T_{2g}(\Gamma_6) \rightarrow {}^4T_{1g}(\Gamma_6)$ and $^4T_{2g}(\Gamma_6) \rightarrow {}^4T_{1g}(^{5/2}\Gamma_8)$ transitions at 6900 and 5950 cm^{-1}, respectively. Similarly, Künzel *et al.*[26] described the luminescence spectra and assigned the highest energy zero-phonon lines for Co^{2+} in $KZnF_3$, K_2ZnF_4, and ZnF_2, these occurring at 6601, 6815, and 6510 cm^{-1}, respectively. Other systems containing six coordinate cobalt(II) for which luminescence has been noted to occur include $LiNbO_3$[28] and several Zr–Ba–La–Al fluoride glasses.[30]

Luminescence has been observed for several acentric four coordinate cobalt(II)-doped systems. For Co^{2+} in $ZnAl_2O_4$, luminescence transitions from the $^2E(^2G)$ state commencing at 11407 and 15723 cm^{-1} were assigned to the $^4T_2$ and $^4A_2$ final states, respectively,[93] whereas luminescence at 77 K from the $^4T_1(P)$ state and commencing at 15160 cm^{-1} has been reported for Co^{2+}-doped $LiGa_5O_8$.[27] More recently, Strek *et al.*[35] demonstrated efficient room-temperature broad-band luminescence in the visible region for the first time, for the Co^{2+}-doped $MgAl_2O_4$ spinel. Band maxima were located at 14 550 and 14 931 cm^{-1}. These bands were both assigned to components of the $^4T_1(P) \rightarrow {}^4A_2$ transition. For cobalt(II)-doped zirconia,[40] this transition occurs at 13 330 cm^{-1}: a band to lower energy, at 10 420 cm^{-1}, was assigned to the $^4T_1(P) \rightarrow {}^4T_2$ transition. Similarly, the Co^{2+}-doped $LiGa_5O_8$[27] and $MgAl_2O_4$[35,41-42] systems also show luminescence bands in the infrared region which have been assigned to transitions between excited states, $^4T_1(P) \rightarrow {}^4T_2$ and $^4T_1(F)$. Several other oxide systems containing four coordinate cobalt(II) ions have been found to luminesce in the infrared region, viz. $LaMgAl_{11}O_{19}$,[37] $ZnGa_2O_4$,[38] $MgGa_2O_4$,[39] and $BaAl_{12}O_{19}$.[105]

Absorption Spectrum of Cobalt(II)-Doped $KCdBr_3$. The low-temperature (14 K) absorption spectrum of the 2% mole $Co^{2+}/KCdBr_3$ system has previously been reported[104] and the *a*-polarized spectrum in the visible region is shown in Figure 1. This spectrum was found to be consistent with a C_s site symmetry for the cobalt(II) dopant ion. The assignments and corresponding excited state energies (up to and including the $^2T_{2g}(H)$ state) are presented in Figure 2. Also given are the energies of the ground state spinor components determined in the present study.

Luminescence from the $^2T_{2g}(H)$ State. The unpolarized low-temperature luminescence spectrum of the present system, after excitation by the 488.0 nm argon-ion line, exhibits a series of sharp lines commencing at 20 029 cm^{-1} (Figure 3). This is the energy assigned to the $^4A''(^4T_{1g}(F)) \rightarrow {}^2A''(^2T_{2g}(H))$ transition in the absorption spectrum.[104] That the luminescence observed is predominantly due to transitions from the $^2A''(^2T_{2g}(H))$ state into the ground state manifold was confirmed using excitation by the 476.5 nm line. A similar luminescence spectrum spanning the same range of photon energies was measured (Figure 3), with the first intense zero-phonon transition again being detected at 20 029 cm^{-1}.

In contrast with the above observations, no sharp luminescence which can be attributed to the $^2A''(^2T_{2g}(H))$ state of cobalt(II)-doped $KCdBr_3$ was detected when the 457.9 nm line was used as the excitation source (Figure 3). Rather, absorption by components of the $^2T_{2g}(H)$ state, assigned to corresponding

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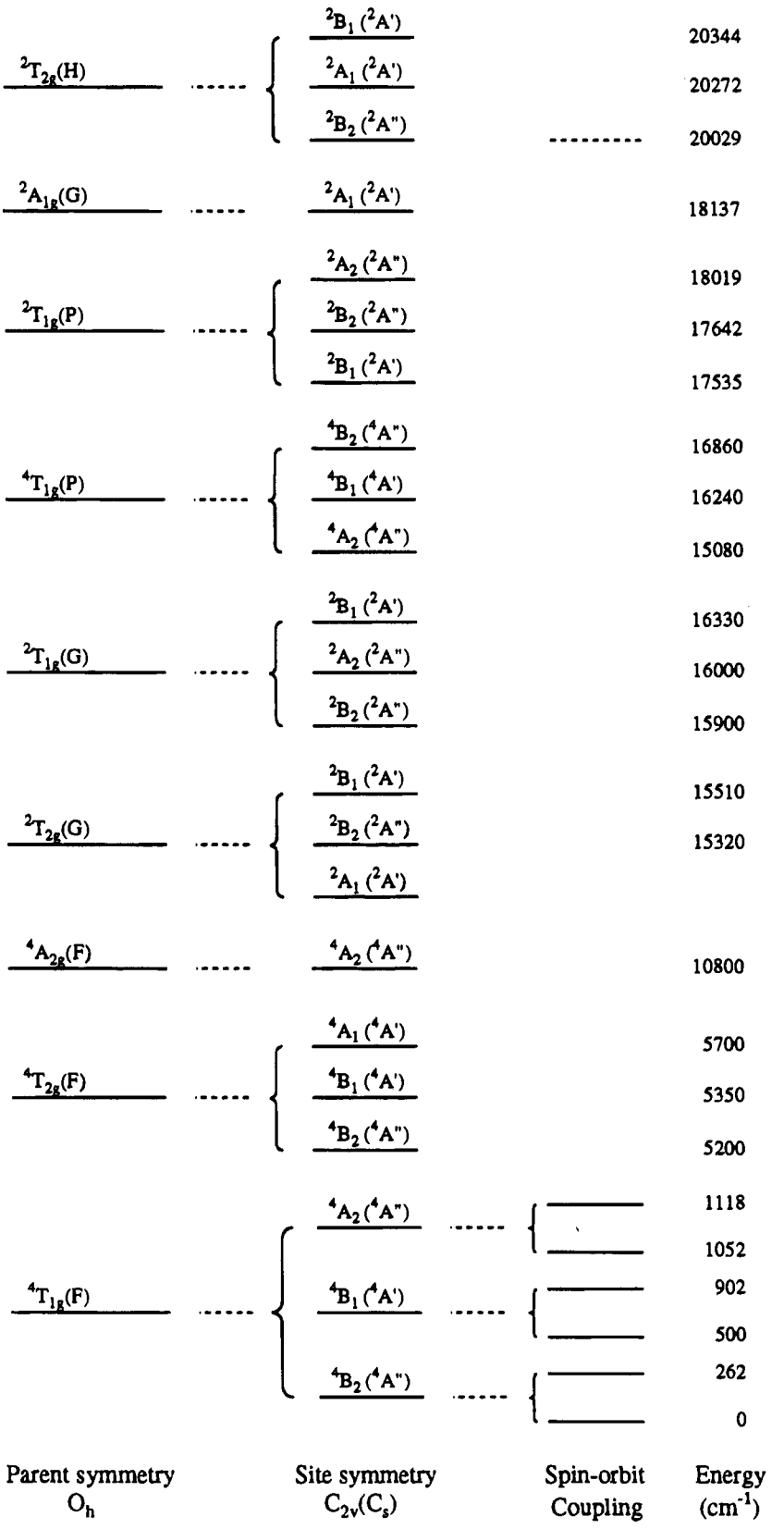

Figure 2. Schematic energy level diagram and energy assignments for the observed transitions of the $Co^{2+}/KCdBr_3$ system.[104] The energies for the ground state spinor states determined in the present study are also given. The luminescing $^2A''(^2T_{2g}(H))$ state of the present study is indicated by a dotted line.

features shown in the expanded region of the spectrum in Figure 1, was observed to be superimposed onto the broad emission background. This suggests either that the 457.9 nm excitation line misses pumping the $^2A''(^2T_{2g}(H))$ state or a cross-relaxation decay process whereby energy is transferred to a neighboring host site. Although the argon-ion 457.9 nm line is also of sufficient energy to excite the $^2A''(^2T_{2g}(H))$ state of the related cobalt(II)-doped $KCdCl_3$ system,[104] no luminescence attributable to this state could be detected.

(i) $^4T_{1g}(F)$ Ground State Splitting. The splitting of the parent $^4T_{1g}(F)$ ground state of six coordinate cobalt(II) halide and doped halide crystals has normally been investigated using

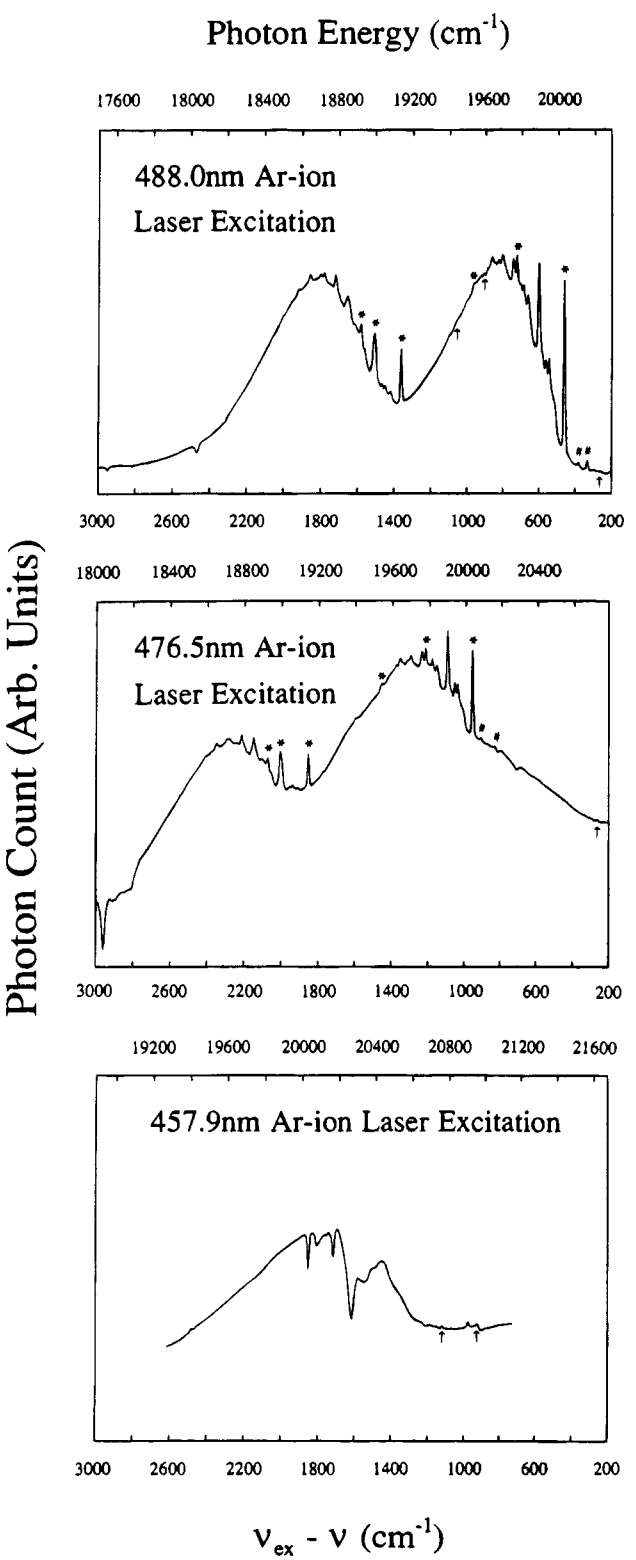

Figure 3. Low-temperature (14 K) unpolarized luminescence/Raman spectrum for an arbitrary single crystal face of 2% Co^{2+}-doped $KCdBr_3$ due to excitation by the 488.0, 476.5, and 457.9 nm argon-ion laser lines. The ground state electronic Raman transitions are indicated by arrows, the zero-phonon single-ion luminescence transitions by stars, and the ion-pair luminescence transitions by cross hatches.

Raman and infrared spectroscopy.[108-114] For crystals of cobalt(II)-doped $KCdBr_3$ several weak electronic Raman transitions were detected. These appear most clearly in the polarized luminescence spectra shown in Figure 4. However, in contrast with previous investigations, the present study is unusual in that the energies of the $^4T_{1g}(F)$ state components were confirmed by sharp luminescence transitions originating in the $^2A''(^2T_{2g}(H))$ state (see below). This compares with the cobalt(II)-doped MgF_2 system for which the ground state splitting was determined solely from the observation of sharp luminescence transitions from the lowest level of the $^4T_{2g}$ state.[92]

Two distinct band envelopes, which have sharp intense origins at 20 029 and 19 127 cm^{-1}, were observed in the low-temperature luminescence spectrum of the $Co^{2+}/KCdBr_3$ crystals (Figures 3 and 4). The separation of these origins suggests that the weak peak with a $(\nu_{ex}-\nu)$ energy of 902 ± 2 cm^{-1} is due to a ground state electronic transition. Furthermore, both this and the peak with a $(\nu_{ex}-\nu)$ energy of 1052 ± 2 cm^{-1} were just as clearly resolved in the 488.0 nm argon-ion line excited luminescence spectra measured at higher temperatures, 50–70 K (Figure 5). Since the resolution of other features was much reduced, this verifies the independence of the weak peaks from the luminescence mechanism of the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ transition. The assignment of the peak at 1052 ± 2 cm^{-1} to an ground state electronic transition was confirmed by the corresponding sharp zero-phonon component at 18 977 cm^{-1} in the luminescence spectrum. A poorly resolved peak with a $(\nu_{ex}-\nu)$ energy of 1118 ± 3 cm^{-1}, is just discernible in the 70 K luminescence spectrum of Figure 5. Assignment of this peak to a ground state electronic transition was established by considering the low-temperature vibronic structure, which corresponds to a number of clear progressions. Neither the peak at 1118 ± 3 cm^{-1} nor the corresponding sharp peak at 18 911 cm^{-1} can be assigned to progressional components associated with lower energy origins. The full assignment of the vibronic structure, to be discussed below, is given in Table 2.

The absence of fundamental vibrational intervals above 200 cm^{-1} suggested that the weak peak with a $(\nu_{ex}-\nu)$ energy of 262 ± 3 cm^{-1} is also due to an electronic transition, and this was confirmed from both its shape retention up to 70 K (Figure 5) and the position of a corresponding sharp luminescence component at 19 766 cm^{-1} (Figures 3 and 4). The other ground electronic state was assigned an energy of 500 ± 3 cm^{-1}, from an analysis of the luminescence fine structure which suggested a vibronic progression with origin at 19 529 cm^{-1}, and associated components with energies of 19 387 and 19 246 cm^{-1}. That the corresponding electronic Raman peak was not observed is unsurprising since, for the luminescence spectra measured using the 488.0 nm excitation line, overlap occurs with the vibronic structure. Furthermore, low laser output powers were employed, ~100 mW. For this reason also, only the electronic Raman transition with $(\nu_{ex}-\nu)$ energy of 913 cm^{-1} was detected in the present study for the related $Co^{2+}/KCdCl_3$ system, in agreement with the finding of Jones and Kuok[108] that this transition is the most intense. Overall, the assignments discussed above are in general agreement with those made for other cobalt(II), halide, and doped halide systems, and the complete ground state spinor assignment is compared with the published data in Table 1.

(ii) Cobalt(II) Pair Transitions. Apart from the zero-phonon line of the $^2A''(^2T_{2g}(H)) \rightarrow {}^4A''(^4T_{1g}(F))$ transition, at 20 029 cm^{-1}, two significantly weaker bands were resolved at 20 099

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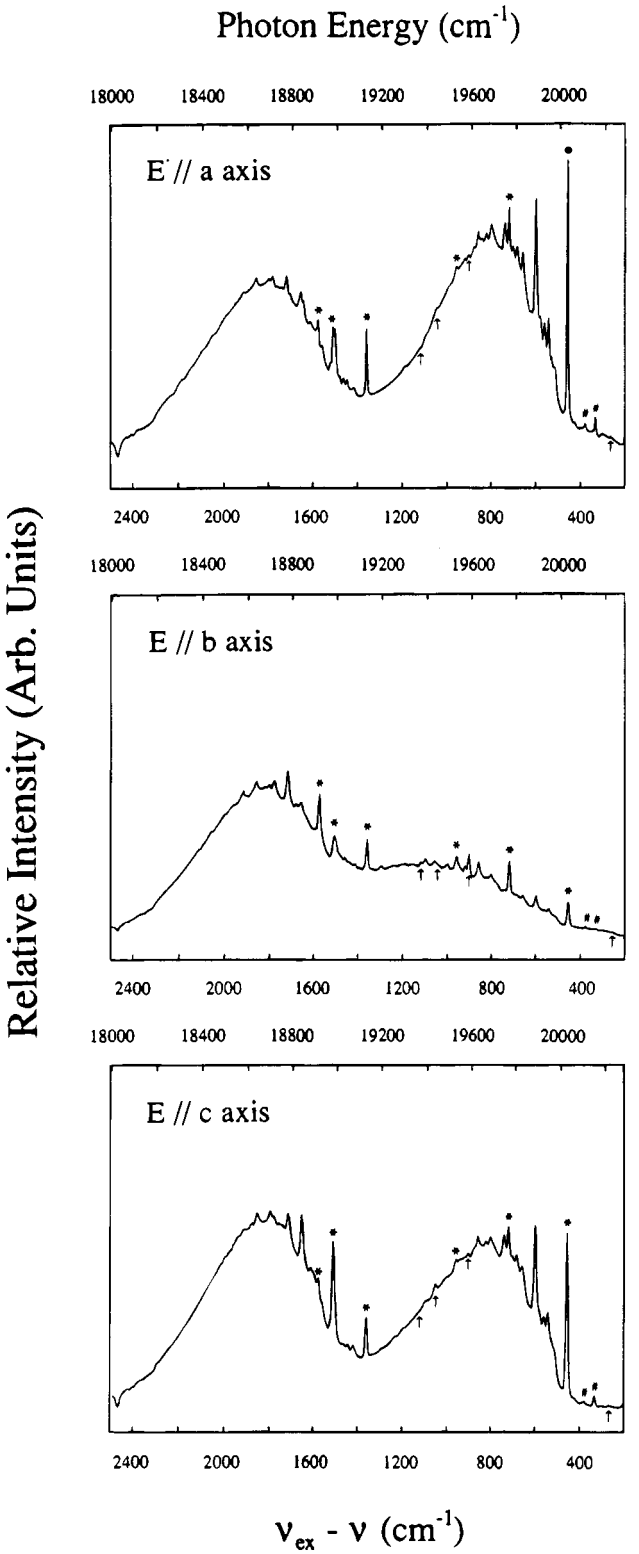

Figure 4. Polarized low-temperature (14 K) luminescence/Raman spectra for a single crystal of 2% Co^{2+}-doped $KCdBr_3$ due to excitation by the 488.0 nm argon-ion line. The ground state electronic Raman transitions are indicated by arrows, the zero-phonon single-ion luminescence transitions by stars, and the ion-pair luminescence transitions by cross hatches. The lower scales of each plot refer to the shift from the excitation line, and the upper scales correspond to the energy of the photons detected.

and 20 146 cm^{-1} (Figure 3). As these energies do not correspond to those of the $^2T_{2g}(H)$ state components in the absorption spectrum,[104] the peaks are tentatively assigned to the same transition but centered upon one ion of the two possible types of Co^{2+} ion pair that can occur in the $KCdBr_3$ host. The

Table 1. Ground State Spinor Energies for Various Six Coordinate Cobalt(II) Halide and Cobalt(II)-Doped Halide Systems (cm^{-1})[a]

$CoCl_2$	$CdCl_2$	$KCdCl_3$	$CsCdCl_3$	$MgCl_2$	$CsMgCl_3$	$MnCl_2$
1115	1088	1188	1070	1130	1379	1108
993	948	1103	947	968	1263	972
962	920	913	873	944	822	938
545	499	531[c]	402[c]	543	472	524
220	235	251[c]	277[c]	212	233	230
$CoBr_2$	$CdBr_2$	$KCdBr_3$	$CsCdBr_3$		$CsMgBr_3$	
1026	995	1118	1129		1231	
941	892	1052	1028		1131	
926	887	902	849		837	
433	394	500	439		448	
257	281	262	260		247	
CoI_2				MgF_2		
956				1398		
895				1258		
882				1087		
327				798		
220				152		

[a] Present study, $KCdBr_3$; ref 92, MgF_2; ref 104, c = calculated; ref 108, $KCdCl_3$, $CsCdCl_3$; ref 109, $MnCl_2$; ref 110, $CdCl_2$, $CdBr_2$, $CsMgCl_3$; ref 113, $CsCdBr_3$, $CsMgBr_3$; ref 114, $CoCl_2$, $CoBr_2$, CoI_2.

crystal structure of $KCdBr_3$, which is isomorphous with that of $KCdCl_3$,[102] contains a double chain of $CdBr_6$ octahedra, and Co^{2+} ion pairs can form within one of the chains or in a staggered arrangement, one cobalt(II) ion in each chain. That the observed peaks are due to luminescence transitions to a component of the ground state is consistent with their decrease in intensity as the temperature is increased to 70 K (Figure 5), which mirrors that of the sharp line at 20 029 cm^{-1}. However, their assignment needs to be confirmed by a more detailed study of the effects of varying the cobalt(II) ion concentration upon the luminescence spectrum. Given that the assignment is indeed correct, and assuming that the intensities of the peaks at 20 029 and 20 146 cm^{-1} are a linear function of the Co^{2+} single ion and ion-pair concentrations, respectively, the ratio of single ions to ion pairs is about 15:1, for the crystals used in this study.

(iii) Assignment of the Vibronic Structure. In addition to the zero-phonon lines in the luminescence spectra of Figures 3 and 4, a great deal of associated vibrational fine structure is resolved, and the improved resolution afforded by the polarized spectra (Figure 4) allowed a detailed analysis of this structure, which is presented in Table 2. In common with other systems, the coupling is expected to be predominantly with first-order phonons.[115] The most notable features are vibrational progressions with as many as four components in a mode having an energy of 141(2) cm^{-1}, assigned to a totally symmetric Co−Br stretching vibration, for which motion probably involves bridging bromide ions. Bailey and Day[116] also report progressional intervals of 135−140 cm^{-1} in the absorption spectra of $CoBr_2$ and $Co^{2+}/CdBr_2$ crystals, which they assigned in a similar manner. By comparison, for $CsCoBr_3$ the A_{1g} phonon was assigned an energy of 168 cm^{-1}.[117] As the energies of the Cd−Br symmetric stretching modes of A_g symmetry in crystals of $KCdBr_3$ were assigned energies of 151, 176, and 189 cm^{-1},[103] a progressional mode energy of 141(2) cm^{-1} would suggest that this vibration is strongly localized on the $CoBr_6$ chromophore. Such a reduction in energy in this case is not unreasonable

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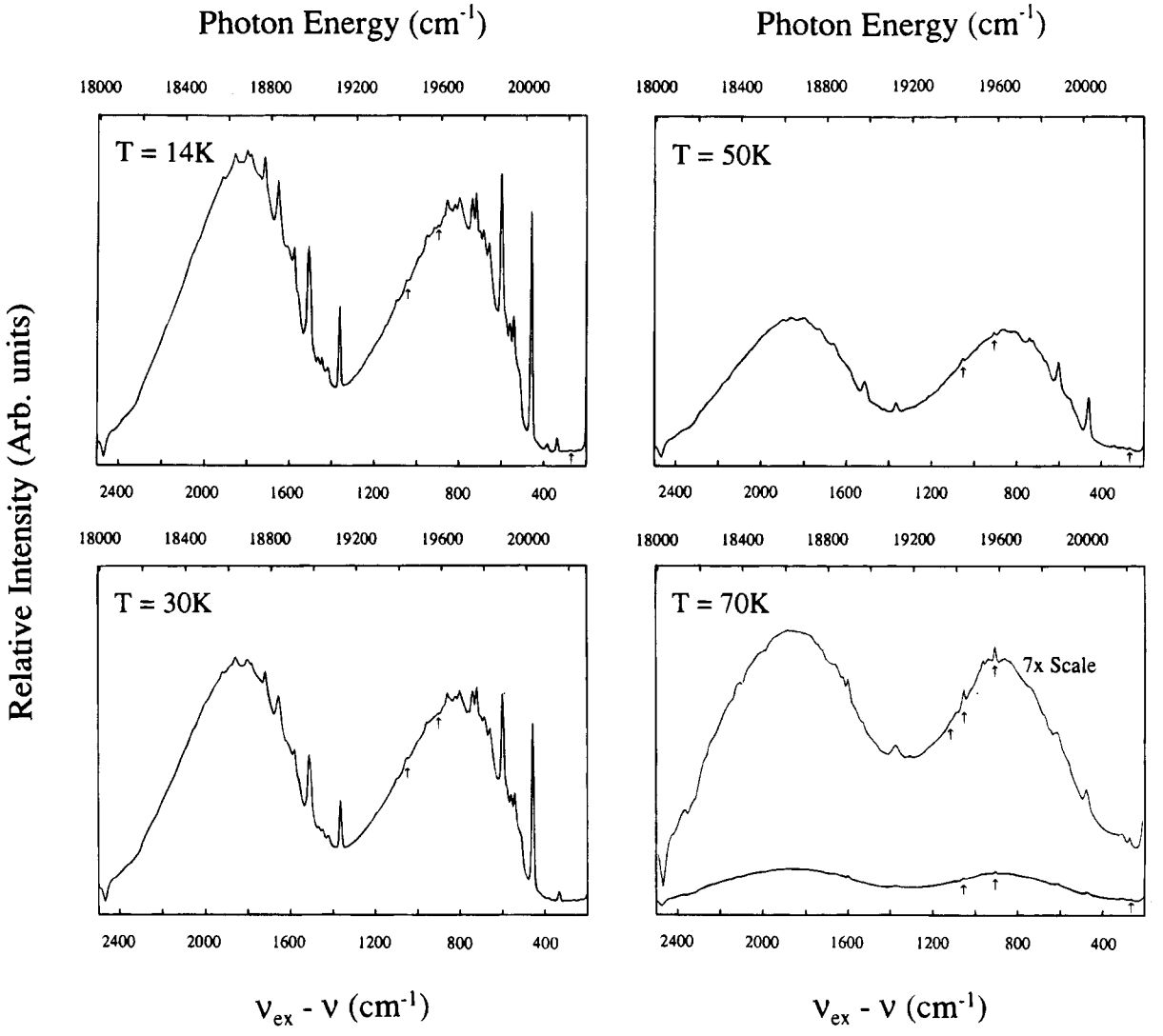

Figure 5. Luminescence/Raman spectrum for a single crystal of 2% Co^{2+}-doped $KCdBr_3$ due to excitation by the 488.0 nm argon-ion line at temperatures of 14, 30, 50, and 70 K. The ground state electronic Raman transitions are indicated by arrows; these are magnified by a factor of 7 in the spectrum measured at 70 K to illustrate their independence from luminescence processes. The lower scales of each plot refer to the shift from the excitation line, and the upper scales correspond to the energy of the photons detected.

because the cobalt(II)−bromide bond lengths are expected to be somewhat longer than in pure systems. However, examination of the Raman spectrum of $KCdBr_3$[103] does reveal a Cd−Br symmetric stretching mode of lower energy, 145 cm^{-1}, although this was assigned B_g symmetry.

The patterns observed in the luminescence spectrum suggest that coupling also occurs with modes assigned energies of 57, 85, 103, and 122 cm^{-1} (Table 2), and this is most apparent in the regions of the spectrum immediately to lower energy than the two sharp origins at 20 029 and 19 127 cm^{-1}. As there are no Raman active vibrations assigned energies close to 57 and 122 cm^{-1},[103] the associated vibrations are probably of *ungerade* character, consistent with at least some intensity in the luminescence spectrum being induced by a vibronic mechanism. In contrast, vibrations at 86 and 103 cm^{-1} assigned B_g and A_g symmetries, repectively, were detected in the Raman spectrum,[103] though this by no means establishes the modes associated with the vibrational fine structure as being one and the same.

Finally, a second totally symmetric Co−Br stretching vibration, associated with terminal bromide ions, might tentatively be assigned an energy of 162(3) cm^{-1}, though coupling with this mode is significantly weaker than that of energy 141(2) cm^{-1} (viz. only a single progressional mode was identified). Again, comparison with the assigned energies of the Cd−Br symmetric stretching modes of A_g symmetry would suggest that such a vibration is probably strongly localized on the $CoBr_6$ chromophore. However, the assignment is also ambiguous since it is not inconceivable that an interval of this magnitude corresponds to a combination of the modes with energies 57 and 103 cm^{-1}. This conclusion is plausible since, from the above discussion, the latter vibration may have A_g symmetry.

(iv) Polarization Properties. In the C_s point group of the cobalt(II) dopant site,[104] the ground state electronic components at 500 and 902 cm^{-1} transform as $^4A'$, all other states being of $^4A''$ symmetry. The absorption spectra indicate that the $^4A''(^4T_{1g}(F)) \rightarrow {}^2A''(^2T_{2g}(H))$ transition is extremely weak in *b*, and most intense in *a*, polarization. In contrast, the peaks assigned to the $^4A''(^4T_{1g}(F)) \rightarrow {}^2A'(^2T_{2g}(H))$ absorption transitions have significant intensity in all polarizations. The polarized luminescence spectra shown in Figure 4 are also consistent with the former observations, the corresponding $^2A''(^2T_{2g}(H)) \rightarrow {}^4A''(^4T_{1g}(F))$ transition being weakest and most intense, in *b* and *a* polarization, respectively. Examination of the spectra also reveals that the electronic Raman peak at 902 cm^{-1}, like the corresponding component at 913 cm^{-1} for the $Co^{2+}/KCdCl_3$ system,[108] is the most intense.

Table 2. Assignment of the Vibrational Fine Structure in the Low-Temperature Luminescence Spectrum of Co^{2+}-Doped $KCdBr_3$ (Using 488.0 nm Excitation)[a]

$(\nu_{ex}-\nu)$	photon energy	ground state energy	assignment
262	20 225		ER
341	20 146		O_1 (pair)
388	20 099		O_1 (pair)
458	20 029	0	O_1
~515	~20 085	~55	$O_1 + 57$
543	19 943	85	$O_1 + 85$
560	19 926	103	$O_1 + 103$
580	19 906	123	$O_1 + 122$
599	19 887	142	$O_1 + 142$
657	19 829	200	$O_1 + 57 + 142$
683	19 803	225	$O_1 + 85 + 140$
702	19 784	244	$O_1 + 103 + 141$
720	19 766	262	O_2
740	19 747	282	$O_1 + 2 \times 141$
798	19 689	340	$O_1 + 57 + 2 \times 141$
803	19 684	345	$O_2 + 85$
822	19 667	362	$O_2 + 103$
841	19 646	383	$O_2 + 121$
860	19 627	400	$O_2 + 140$
902	19 585		ER
920	19 567	462	$O_2 + 57 + 142$
939	19 548	481	$O_1 + 57 + 3 \times 141$
958	19 528	500	O_3
1000	19 486	542	$O_2 + 2 \times 140$
1054	19 432		ER
1058	19 428	600	$O_3 + 103$
1099	19 387	641	$O_3 + 142$
1120	19 366	662	$ER/O_3 + 162$
1158	19 328	700	$O_3 + 57 + 142$
1198	19 298	740	$O_3 + 103 + 140$
1240	19 246	782	$O_3 + 2 \times 141$
1297	19 189	839	$O_3 + 57 + 2 \times 141$; O_4 (pair?)
1360	19 127	902	O_4
1417	19 070	960	$O_4 + 57$
1445	19 042	987	$O_4 + 85$
1464	19 023	1006	$O_4 + 103$
1482	19 005	1024	$O_4 + 122$
1500	18 987	1042	$O_4 + 140$
1510	18 977	1052	O_5
1522	18 963	1064	$O_4 + 162$
1560	18 927	1102	$O_4 + 57 + 142$
1576	18 911	1118	O_6
1601	19 886	1143	$O_5 + 85$; $O_4 + 103 + 141$
1644	18 843	1186	$O_4 + 2 \times 142$
1653	18 835	1194	$O_5 + 142$
1658	18 830	1199	$O_6 + 85$
1679	18 809	1220	$O_6 + 103$
1702	18 785	1244	$O_4 + 57 + 2 \times 142$; $O_6 + 122$
1717	18 770	1259	$O_6 + 141$
1742	18 745	1284	$O_5 + 85 + 142$; $O_4 + 103 + 2 \times 141$
1777	18 710	1319	$O_6 + 57 + 142$
1797	18 690	1339	$O_5 + 2 \times 142$
1801	18 696	1343	$O_6 + 85 + 140$
1858	18 629	1400	$O_6 + 2 \times 141$
1903	18 584	1445	$O_5 + 103 + 2 \times 142$ (?)
1917	18 571	1458	$O_6 + 57 + 2 \times 141$
1960	18 528	1501	$O_6 + 103 + 2 \times 141$
1998	18 490	1539	$O_6 + 3 \times 141$
2056	18 432	1597	$O_6 + 57 + 3 \times 141$
2111	18 377	1652	$O_6 + 103 + 3 \times 141$; $O_6 + 122 + 3 \times 141$

[a] All energies are in cm^{-1}. O_1 to O_6 refer to transitions to ground state electronic origins. ER = Electronic Raman transition.

(v) Band Shape Analysis. The clear resolution of two luminescence band envelopes for the $Co^{2+}/KCdBr_3$ system indicates that the electron–phonon coupling constant, or Huang–Rhys factor, is smaller for transitions to the ground state from the $^2T_{2g}(H)$, than the $^4T_{2g}$, state. This follows since, normally, the spectra of cobalt(II)-doped systems in the region of $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ emission exhibit a single band.[26,31,92,106-107] From the intensity distribution, I_n, within a totally symmetric vibrational progression, the Huang–Rhys parameter S can be calculated by

$$I_n/I_0 = S^n/n!$$

where n is the number of a_g quanta involved. The intensities of the first three members of the progression of the highest energy $^2A''(^2T_{2g}(H)) \rightarrow {}^4A''(^4T_{1g}(F))$ luminescence transition, at 20 029, 19 887, and 19 747 cm^{-1}, give a calculated value of 0.55 ± 0.05 for S. This compares with values for S of 2.5 ± 0.2 and 5.6 ± 0.5 estimated by Reber and Güdel[92] for the lowest energy $^3T_{2g} \rightarrow {}^3A_{2g}$ luminescence transition of nickel(II)-doped $CsMgCl_3$ and $CsMgBr_3$ crystals, respectively, and which are expected to be similar for the $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ transitions of the corresponding cobalt(II)-doped systems.

(vi) General Considerations. The recent focus upon new transition metal doped hosts as potential broad-band tunable lasers has targeted those materials which luminesce at, or near to, room temperature as being most promising for further investigation.[56,61] In this respect, the effect of temperature upon the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ luminescence was investigated and spectra obtained at temperatures up to 70 K are shown in Figure 5. Clearly, nonradiative decay processes begin to dominate at relatively low-temperatures causing a rapid drop in luminescence intensity and this is consistent with the low energy, 141(2) cm^{-1}, of the ν(Co–Cl) stretching vibration expected to participate strongly in these processes.[118] Therefore, the present spin-forbidden luminescence is probably not a suitable candidate for the further investigation of laser action, even if the cobalt(II) concentration was decreased or the quality of the $Co^{2+}/KCdBr_3$ crystals improved by more rigorous control of the growth conditions.

As the energy gap from the $^2A''(^2T_{2g}(H))$ state to the next lower $^2A'(^2A_{1g}(G))$ state[104], 1892 cm^{-1}, corresponds to more than thirteen quanta of the ν(Co-Cl) stretching vibration, this probably accounts for the observation of luminescence from the $^2A''(^2T_{2g}(H))$ state in the first instance, since the break-even point between radiative and non-radiative processes typically occurs when the energy gap can be bridged by about six vibrational quanta.[118] In contrast for the well studied Co^{2+}/MgF_2 system, the "effective" energy of such a vibration will be similar to that of the host A_{1g} phonon,[119] 410 cm^{-1}. Since in the stronger ligand field of the fluoride host the energy gap is expected to be smaller, the transition will involve only three to four vibrational quanta and non-radiative decay from the $^2T_{2g}(H)$ state will dominate.

Finally, in considering the present system as a potential laser material, examination of the emission intensity down to an energy of ~14 000 cm^{-1} did not reveal luminescence originating from other metastable states of the cobalt(II) ion. This, however, does not preclude further studies which might detect luminescence from the lowest energy $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ transition or search for luminescence transitions between metastable states, e.g. $^2A''(^2T_{2g}(H)) \rightarrow {}^4A''(^4T_{1g}(P))$, as such transitions have been observed for Co^{2+} ions in the tetrahedral sites of the $LiGa_5O_8$[27] and $MgAl_2O_4$ hosts.[35,41-42] Site-selective pumping of various cobalt(II) sites might also be considered in crystals having a range of cobalt(II) concentrations. Studies of this and the above kind

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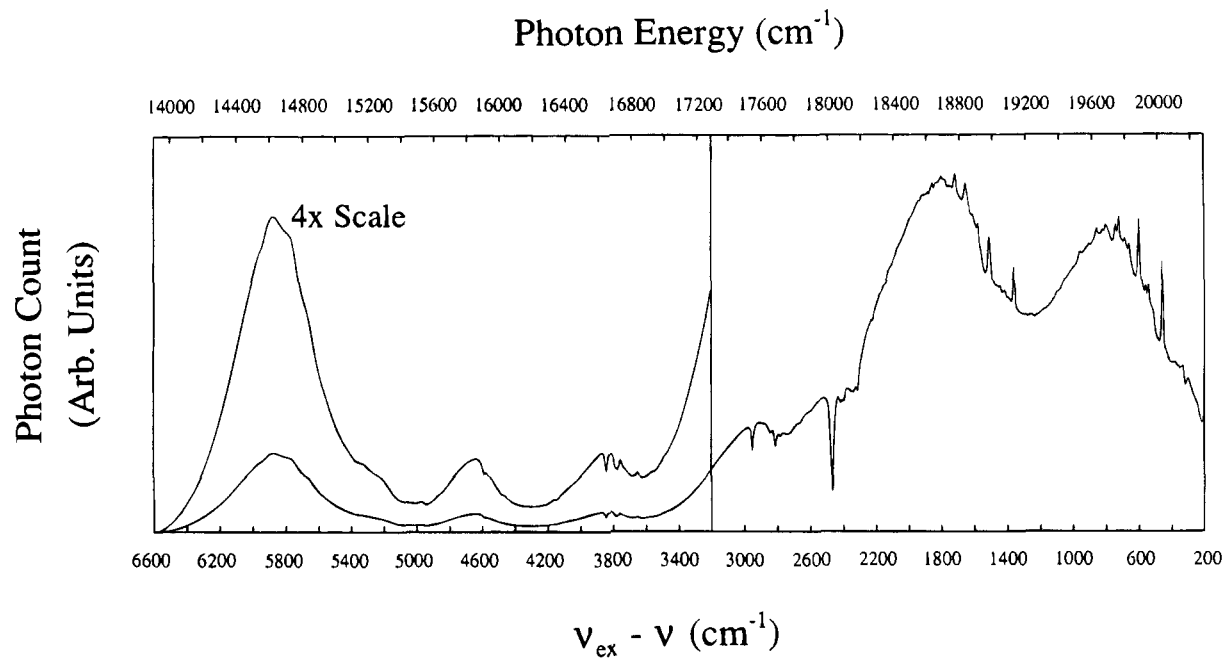

Figure 6. Unpolarized low-temperature luminescence (14 K) for a single crystal of 2% Co^{2+}-doped $KCdBr_3$ due to excitation by the 488.0 nm argon-ion line. This spectrum was measured after "aging" well-polished crystal faces (cf. the corresponding measurement in Figure 3). The region of the spectrum shifted more than 3500 cm^{-1} from the excitation line is expanded by a factor of 4.

by the present authors were not possible due to equipment limitations, viz. the excitation source, the diffraction grating, and the detector.

Host Crystal, Impurity, and Surface Site Luminescence. The spectrum due to the luminescence from the $^2A''(^2T_{2g}(H))$ state is superimposed upon that due to other emission processes. For Co^{2+}-doped systems, luminescence due to Ni^{2+} impurities has also been identified[92] and may contribute strongly to the background intensity in the present case. In addition, luminescence of the host material is quite likely since bands assigned to emission from Br_2^{2-} centers at 3.3, 2.0, and 1.8 eV (i.e. 26 600, 16 100, and 14 500 cm^{-1}) have been observed for the related host material $CsCdBr_3$.[120] Finally, the present crystals are slightly hygroscopic and clearer polished crystal surfaces were observed to "cloud" over a period of time. This may produce new sites at which emission occurs.

The competition between absorption and emission processes is an important factor if there is significant overlap between the absorption and luminescence bands, as self-absorption often degrades the performance of transition metal doped crystals as laser materials.[56] For the $Co^{2+}/KCdBr_3$ system self-absorption has only a small effect on the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ transition, being apparent on the low-energy tail of the lower energy band envelope (Figures 3 and 6). As part of the self-absorption process, there is, in general, a decrease in the background emission intensity which manifests itself as "holes" due to sharp states of the cobalt(II) ion. The energies of the most prominent "dips" in Figure 6 (at 18 019, 17 642, 17 535, 16 701, 16 644, 16 334, ~16 000, and 15 897 cm^{-1}) correspond to spin-forbidden transitions to components of the $^2A_{1g}(G)$, $^2T_{1g}(P)$, and $^2T_{1g}(G)$ states, which occur in the absorption spectrum (Figure 1). Similar absorption "dips" have been noted in the investigation of the $Co^{2+}/MgCl_2$ system;[121] "holes" due to absorption by components of the $^2A_{1g}(G)$ and $^2T_{1g}(P)$ states have also been observed for the $Co^{2+}/KCdCl_3$ system. The size of the "dips" was found to be dependent upon the position of the laser beam relative to the crystal surface, the background emission intensity, and the quality of the crystal surface.

A comparison of the background intensity for the plots of Figure 3 suggests a broad underlying emission band centered at ~20 200 cm^{-1} in the spectrum obtained using 476.5 nm excitation. This is probably due a change in the quality of the crystal surface, as the same crystal was used for both measurements. The "aging" of highly polished crystal faces in the atmosphere also caused the absorption "dips" to become more pronounced relative to the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ luminescence bands (Figure 6). Presumably, this is due to the effects of surface degradation such as oxidation and water adsorption. Not only can new luminescing species be produced in the near-surface layers of the crystal, but surface degradation will cause diffusion of the incident laser beam, reducing the excitation energy at any one site and increasing the relative efficiency of the absorption process.

The most interesting feature of Figure 6 is the appearance of a broad-band luminescence transition commencing at ~15 200 cm^{-1} which seems to show a weakly resolved vibronic progression in a mode of energy ~100 cm^{-1} and an intensity maximum at ~14 600 cm^{-1}. This band cannot be due to a nickel(II) impurity since there is no corresponding absorption band for the analogous $Ni^{2+}/KCdBr_3$ system.[122] Furthermore, it cannot be assigned to a $^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$ transition of the cobalt(II) ion. Close examination shows that several of the sharp "dips" mentioned above are superimposed upon broad-band absorptions corresponding to the $^4A''(^4T_{1g}(F)) \rightarrow {}^4A'$, $^4A''(^4T_{1g}(P))$ absorption transitions of the $Co^{2+}/KCdBr_3$ system which occur at 16 240 and 16 860 cm^{-1}, respectively (Figure 1). In addition, luminescence from the lowest energy $^4A''(^4T_{1g}(P))$ component, which has a maximum at 15 080 cm^{-1} in the absorption spectrum (Figure 1), is expected to commence at ~14 500 cm^{-1} and have an approximate mirror image symmetry to the absorption band. Further examination of Figure 6 also suggests that since the structure on the observed feature cannot be detected to lower energies than ~14 500 cm^{-1}, it appears

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likely that the pattern observed can be also be explained by absorption, into the lowest energy $^4A''(^4T_{1g}(P))$ component. Similarly, deviations in the photon count at 15 200, ~15 300, and 15 511 cm^{-1} may be due to absorption, by components of the $^2T_{2g}(G)$ state.

The source of the emission intensity upon which is superimposed absorption into the $^4T_{1g}(P)$ manifold could be due to a Br_2^{2-} center; the luminescence properties assigned to this species in $CsCdBr_3$ correspond to bands centered at 14 500 and 16 100 cm^{-1}.[118] However, it is not inconceivable that the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{2g}$ excited state luminescence transition is being observed. Examination of the energy level diagram in Figure 2 indicates that this transition would be expected to have maximum absorption at about 14 800 cm^{-1}. If this were the case it is likely that luminescence from the $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ transition can also be detected.

Conclusions

The present study of $Co^{2+}/KCdBr_3$ has demonstrated the first example of luminescence originating in the $^2T_{2g}(H)$ state of the cobalt(II) ion. The vibrational fine structure associated with the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ transition has allowed the energies of the ground state spinor components to be determined and for several of these, confirms the observation of the corresponding weak electronic Raman transitions. Furthermore, the observed spectra were found to be dependent upon the energy of the laser excitation line, the state of degradation of the crystal surfaces, and the presence of other luminescing sites within the crystal bulk.

Although the $^2A''(^2T_{2g}(H)) \rightarrow {}^4T_{1g}(F)$ transition does not appear to be a good candidate for sustaining laser action at room temperature, investigations of the luminescence due to the $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ transition are worth pursuing for both the present system and the analogous cobalt(II)-doped $KCdCl_3$ material.

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