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Exchange-coupled Cr^{3+} pairs in CsCdBr_3 : an optical and Raman study

F Pellé†, Ph Goldner† and O Pilla‡

† Laboratoire de Physicochimie des Matériaux, UPR 211–CNRS, 1 Place Aristide Briand, 92190 Meudon–Bellevue, France

‡ Dipartimento di fisica, Università di Trento, I38050 Povo, Trento, Italy

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Abstract. The absorption and emission spectra of Cr^{3+} impurities in the unidimensional host lattice CsCdBr_3 are presented. The observed features are assigned to Cr^{3+} –vacancy– Cr^{3+} exchanged-coupled centres whose axis is parallel to the crystallographic c axis. Since the deduction of the exchange parameters from the optical spectra is not unambiguous a different approach is proposed. Impurity-induced resonant Raman scattering allows a direct evaluation of the ground state splitting of the pairs and therefore an estimate of the strength of the exchange interaction.

1. Introduction

The spectroscopic study of exchange-coupled pairs (ECP) in crystals is in general a difficult task because, in order to obtain suitable pair concentration, the doping concentration must be greatly increased. But in addition to the pairs, many unwanted centres are produced, like isolated impurities, pairs with different symmetries and aggregates (Kisliuk *et al* 1969, Larkin *et al* 1973, Fairbank and Klauminzer 1973). A model system for this situation is ruby. Many works have been published on the identification of the pair transitions and on their theoretical study in this material (Kisliuk *et al* 1969, Nikoforov and Cherepanov 1971, Naito 1973). To overcome the difficulties related to the coexistence of several optically active centres, a family of binuclear materials has been proposed, where the magnetic ions enter stoichiometrically and not as a dopant. The structure of these systems is of the type $\text{A}_3\text{B}_2\text{X}_9$ (where $\text{A} = \text{Cs}^+, \text{Rb}^+$; $\text{B} = \text{Cr}^{3+}$; $\text{X} = \text{Cl}^-, \text{Br}^-$) and consist of binuclear $(\text{Cr}_2\text{Br}_6)^{3-}$ units in which the separation between two B ions is half the distance between two B ions belonging to different units (Wessel and Ijdo 1957); these distances are 3.3 Å and 7.4 Å respectively in $\text{Cs}_3\text{Cr}_2\text{Br}_9$. Moreover, in this case the Cr^{3+} pair has high symmetry (D_{3h}) allowing a relatively simple interpretation of the optical spectra by means of group theory. Even in this more favourable case, however, it is necessary to make some approximation, i.e. to neglect the interaction between pairs (which is in general small with respect to the intra-unit interaction) and all the collective effects (Leuenberger *et al* 1983). In any case, the deduction of the exchange parameters is not straightforward and requires a detailed study of Zeeman spectroscopy, EPR and emission spectra.

In this paper we present a study on a system in which the advantages of both previous cases are present. In fact, even at very low concentration of M^{3+} ions, only M^{3+} – M^{3+} ECP are present because of the peculiar structure of the host lattice and thus it is possible, at low concentration, to neglect the inter-pair interaction. The crystal we have chosen is the

uniaxial CsCdBr₃ in which the magnetic ions Cr³⁺ substitute for Cd²⁺ in a slightly distorted cubic site (site symmetry C_{3v}). The structure of this compound has been fully described elsewhere (McPherson *et al* 1970). EPR measurements showed that trivalent ions enter this lattice to form antiferromagnetic ECP following the sequence Cr³⁺-vacancy-Cr³⁺ (which is electrically neutral) along the hexagonal *c* axis of the crystal. The complex consists of three octahedra of bromine ions sharing faces with a Cd²⁺ vacancy in the central octahedron (the symmetry of the pair being D_{3d}). The Cr³⁺-Cr³⁺ separation is 6.0 Å and the entity Cr³⁺-vacancy-Cr³⁺ is greatly favoured during the crystallization (McPherson *et al* 1978). Due to this characteristic, CsCdBr₃ is an excellent candidate on which to study both the spectroscopy of the ECP and, by varying the Cr³⁺ concentration, the pair-pair interactions.

2. Experimental details

Absorption measurements were carried out on a Cary 17 spectrometer. Emission was excited by a Coherent CR12 Ar⁺-ion laser. A Jobin-Yvon double monochromator and photomultiplier (S1 response) were used in detection. For lifetime measurements the excitation was provided by a pulsed N₂ laser (pulse width 5 ns); the signal was analysed by a boxcar integrator (PAR model 162). A variable temperature cryostat was used for low temperature measurements. The Raman set up consisted in a model 164 Ar⁺-ion laser plus a Jobin-Yvon double monochromator. A photon counting detector was used.

Large single crystals were grown from the melt by the Bridgman method after drying the starting products in a bromine atmosphere. The concentration of Cr³⁺ ions in the samples studied was 0.5%. The crystals are green, stable in air and easily cleaved along the crystallographic *c* axis.

3. Results

Figure 1 shows the 9 K polarized absorption spectrum of this material. The two main bands peaking at 12 080 and 16 700 cm⁻¹ are assigned to the spin-allowed pair transitions for the ⁴A₂ × ⁴A₂ ground state to the ⁴A₂ × ⁴T₂, ⁴A₂ × ⁴T₁^(1a) excited levels respectively. In addition to the main features weaker structures are observed in the spectral ranges 13 900–14 900 and 18 500–20 000 cm⁻¹ which are due to the spin forbidden transitions to the ⁴A₂ × ²E, ⁴A₂ × ²T₁ and ⁴A₂ × ²T₂ ECP excited levels (figure 2). In this notation, (⁴A₂ × ²E) stands for the state in which one ion of the pair is in its ground state (⁴A₂) and the other one is in the excited (²E) level. It should be noted, however, that strictly speaking, since the symmetry of the pair is D_{3d}, the use of the cubic notation is not fully appropriate. As usual, it is retained for the sake of simplicity. On increasing the temperature the intensity of the two main bands increases, while the small structures vanish. The splitting between the π and σ components of the bands reflects the axial character of the absorption centre.

Under visible excitation a weak broad and unstructured emission band is observed (figure 3). This emission is centred at 10 000 cm⁻¹ (FWHM = 1200 cm⁻¹) at 10 K. The intensity of fluorescence increases by a factor of two in the 10–130 K temperature range. Increasing further the temperature results in a quenching of the emission intensity and the fluorescence is not detected at temperatures higher than 230 K.

The decay time of the emission at 10 K is 30 μs and shortens to 5 μs at 200 K. This value is consistent with the lifetime of a ⁴T₂ emission (in a low field site) which is usually in the microsecond range. For instance for the isolated Cr³⁺ impurity in KZnF₃ (Pilla *et*

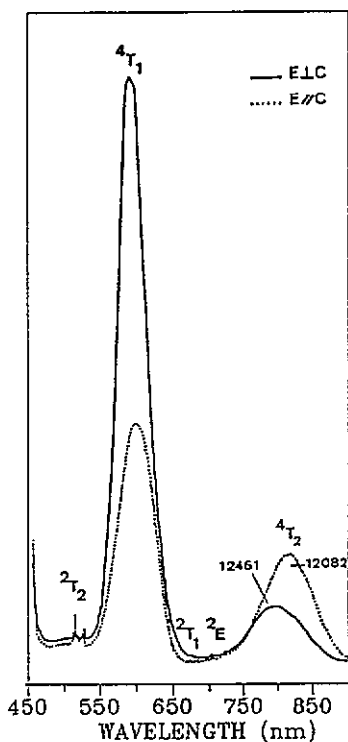


Figure 1. Polarized absorption spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ ($T = 9$ K).

al 1988) ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ lifetime at liquid helium temperature was found to be $460 \mu\text{s}$. In the system under study, we are dealing with pairs, and the lifetime is expected to be shorter (Kisliuk *et al* 1969).

The splitting of the Cr^{3+} ground state has been directly measured by means of resonant-impurity-induced Raman scattering experiments. It should be noted that signal was detected only using the 514.5 and 501.7 nm lines of the Ar^+ -ion laser (figure 4(a)). Using the other lines at higher energy only the usual Raman signal from the host lattice modes (Pilla *et al* 1987) is observed (figure 4(b)). As can be seen on figure 2(b), the 514.5 and 501.7 nm laser lines are nearly resonant with the ${}^4\text{A}_2 \times {}^2\text{T}_1$ excited level of ECP, this yields an increase in the electronic Raman spectra allowing the observation of two structured bands peaking at 29 and 51 cm^{-1} from the laser line. At higher temperatures the corresponding Stokes transitions are observed. The structure of the peaks reflects the fine splitting of the ground state manifold of ECP.

4. Discussion

Usually, the exact sequence of the sublevels involved in the different transitions can be deduced from the study of the polarized absorption spectra as a function of temperature and under a magnetic field. This is a difficult approach because the ECP levels are highly structured (Dean and Maxwell 1982, Johnstone *et al* 1981, Briat *et al* 1977). The analysis of the splittings in the optical spectra is difficult, because in the presence of electronic orbital degeneration, the effective Hamiltonian is more complicated, requiring the introduction of several exchange parameters, and, in addition, the Jahn–Teller effect is also expected to

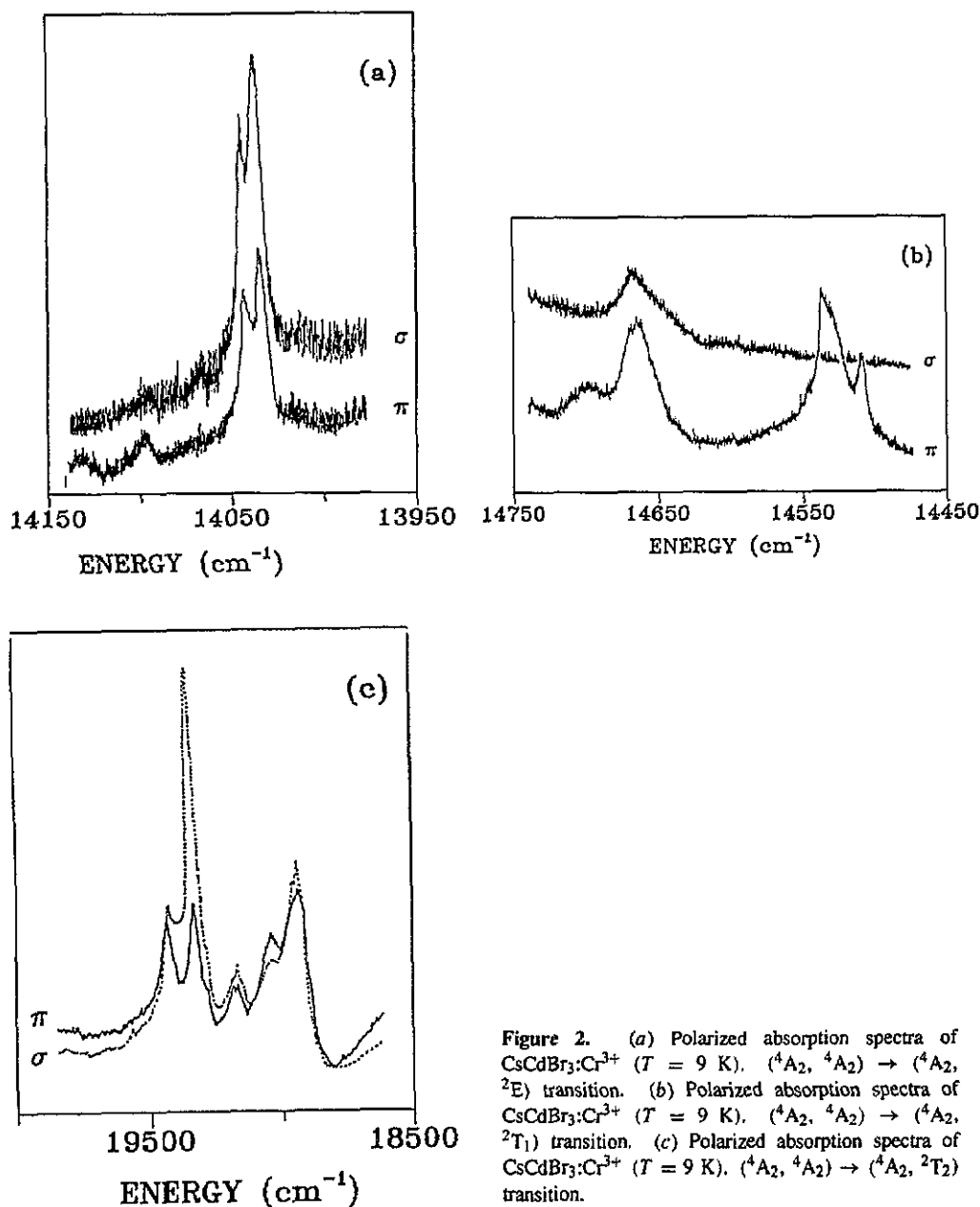


Figure 2. (a) Polarized absorption spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ ($T = 9$ K). (${}^4A_2, {}^4A_2 \rightarrow {}^4A_2, {}^2E$) transition. (b) Polarized absorption spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ ($T = 9$ K). (${}^4A_2, {}^4A_2 \rightarrow {}^4A_2, {}^2T_1$) transition. (c) Polarized absorption spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ ($T = 9$ K). (${}^4A_2, {}^4A_2 \rightarrow {}^4A_2, {}^2T_2$) transition.

quench the exchange interaction. By means of EPR it is possible to determine the ground state fine structure, but also in this case (McPherson *et al* 1978) difficulties arise from the fact that the lowest state ($S_g = 0$) (antiferromagnetic coupling) is not EPR active, and a detailed study in temperature is required. The direct measurement of the splitting from the emission spectra as in ruby (Kisliuk *et al* 1969) is not possible in these systems, since Cr^{3+} in low crystal field emits a broad unstructured band.

In view of the great similarity between the absorption spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ and

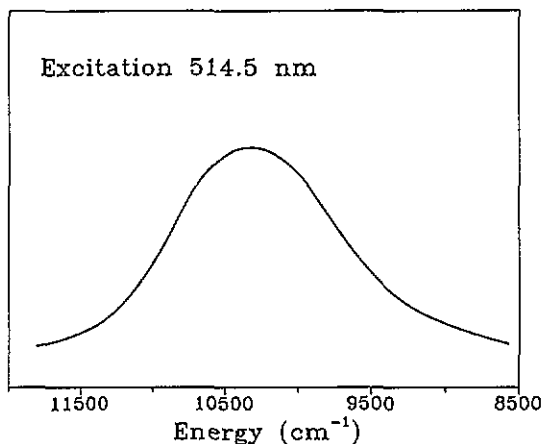


Figure 3. Emission spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ ($T = 9$ K, excitation in the ${}^4\text{T}_1$ level).

the cited binuclear systems we have not attempted any further investigation of the ECP absorption spectra under magnetic field. Moreover in this case the only transition suitable for this kind of study would be the ${}^4\text{A}_2 \times {}^4\text{T}_2$ transition, the other fine structures (${}^4\text{A}_2 \times {}^2\text{E}$, ${}^4\text{A}_2 \times {}^2\text{T}_1$) being too weak. Nevertheless it is possible to deduce some information from the polarized absorption at different temperatures.

Diagonalizing the d^3 matrix (Eisenstein 1961) with a value of $10 Dq$ appropriate for the absorption (12080 cm^{-1}), we obtain for the Racah parameters B and C values of 670 and 3020 cm^{-1} respectively. This yields a reduction factor K from the free-ion value of 0.71 . This can be used as first approximation to get the effective spin-orbit constant $\xi^* = K \xi_{\text{free ion}} = 195 \text{ cm}^{-1}$. The use of cubic d^3 matrix is not fully appropriate in this case since we are dealing with Cr^{3+} pairs in a non-cubic environment. Owing to the small distortion from O_h symmetry it is usual to take, as a starting point for further studies the values of the parameters so obtained. As already pointed out in the literature (Dubicki *et al* 1977) the electric dipole selection rules for an ion in a distorted O_h (C_{3v} local symmetry) apply also for exchange-induced electric dipole transitions. This allows an assignment of the polarized bands in the 12000 cm^{-1} range to the ${}^4\text{A}_2 \times {}^4\text{A}_1$ (12100 cm^{-1}) and ${}^4\text{A}_2 \times {}^4\text{E}$ (12500 cm^{-1}) split components of the ${}^4\text{A}_2 \times {}^4\text{T}_2$ band in ($E//c$) and ($E \perp c$) polarization respectively. The splittings arise from the first-order trigonal field; for the ${}^4\text{A}_2 \times {}^4\text{T}_2$ the distortion parameter v is found to be -250 cm^{-1} , well within the range of values reported in the literature (Dubicki *et al* 1977). However, the intensity of the (${}^4\text{A}_2 \times {}^4\text{A}_1$) \rightarrow (${}^4\text{A}_2 \times {}^4\text{A}_1$) transition does not obey these selection rules since it is observed in σ polarization. The same effect has been earlier observed in $\text{Cs}_3\text{Cr}_2\text{X}_9$ systems ($X = \text{Cl}^-$, Br^-) and attributed to a vibronic mechanism (Dubicki *et al* 1977) which enhances the oscillator strength.

The temperature dependence of bandwidths (Γ) and intensities of the two main features follows the well-known law

$$\Gamma, I \propto \coth(h\omega_{\text{eff}}/kT)$$

yielding values for the $h\omega_{\text{eff}}$ of 145 cm^{-1} , well between the phonon energies of the host lattice (Pilla *et al* 1987).

Let us consider now the weaker structures assigned to spin-forbidden transitions. Although, as already pointed out, MCD measurements as a function of temperature are necessary for a complete understanding of the observed structures, we will discuss

qualitatively the experimental spectra in the light of the previous reported data on similar systems (Dean and Maxwell 1982, Johnstone *et al* 1981, Briat *et al* 1977, Eisenstein *et al* 1961, Dubicki *et al* 1977). In table 1, we report the energies of the main features for the three spin-forbidden transitions.

Table 1. Energies of spin-forbidden absorption lines observed in CsCdBr₃:Cr³⁺ ($T = 9$ K).

Transition	Energy (cm ⁻¹)
${}^4A_2 \times {}^4A_2 \rightarrow {}^4A_2 \times {}^2E$	14 043
	14 035.6
${}^4A_2 \times {}^4A_2 \rightarrow {}^4A_2 \times {}^2T_1$	14 505
	14 526
	14 535
	14 663
	14 669
${}^4A_2 \times {}^4A_2 \rightarrow {}^4A_2 \times {}^2T_2$	18 835
	18 905
	18 920
	18 976
	19 026
	19 139
	19 158
	19 174
	19 193
	19 270
	19 315
19 411	
19 514	
19 567	

The fine structure ascribed to the spin-forbidden transitions ${}^4A_2 \times {}^4A_2 \rightarrow {}^4A_2 \times {}^2E$ and ${}^4A_2 \times {}^4A_2 \rightarrow {}^4A_2 \times {}^2T_1$ has been studied at low temperature (9 K) and in polarized light.

Concerning the ground state, EPR data (McPherson *et al* 1978) indicate that Cr³⁺ pairs in CsCdBr₃ are antiferromagnetically coupled, this gives a series of four levels labelled according to the total spin S , $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$ in order of decreasing energy. The energy difference with respect to the $|0\rangle$ state can be expressed as a function of J , the superexchange parameter, and of j which accounts for magnetostriction effects (Dubicki and Tanabe 1977):

$$|0\rangle - |1\rangle = J + 6.5j \quad |0\rangle - |2\rangle = 3J + 13.5j \quad |0\rangle - |3\rangle = 6J + 9j. \quad (1)$$

Since J is small in these compounds ($J = -15$ cm⁻¹, McPherson 1978), we can assume at low temperature a very weak population of the levels of the ground multiplet except for $|0\rangle$ and $|1\rangle$.

The splittings of pair levels under different perturbations are summarized in table 2 and selection rules according to pair symmetry can be found in table 3 (for levels of interest only).

(i) (${}^4A_2 \times {}^4A_2$) \rightarrow (${}^4A_2 \times {}^4E$) transition. As shown in figure 2(a) we observed two lines at 14 043 and 14 035.6 Å in σ and π polarizations. We conclude from tables 2 and 3 that the observed absorption lines correspond to transitions from the ${}^3A_{1g}$ level to the 3E_u

and ³E_g components of the (⁴A₂ × ²E) state. This interpretation gives a value of -8 cm⁻¹ for *J*.

(ii) (⁴A₂ × ⁴A₂) → (⁴A₂ × ⁴T₁) transition. Observed lines and their polarizations are reported in table 4. We deduce from these results the correspondence between the observed levels and the theoretical transitions are shown in table 4.

The two first transitions give *J* = -10 cm⁻¹ and the two following *J* = -9 cm⁻¹.

Table 2. Cr³⁺ pair states symmetry in CsCdBr₃.

O _h	H ₁ + H ₂	H ₁₂	H _{ex}	H _{SO}
	C _{3v}	D _{3d}		
(⁴ A _{2g} , ⁴ A _{2g})	(A ₂ , A ₂)	A _{1g}	³ A _{1g} ¹ A _{1g}	A _{2g} + E _u A _{1g}
(⁴ A _{2g} , ² E _g)	(A ₂ , E)	E _u E _g	³ E _u ³ E _g	A _{1g} + A _{2g} + E _g + E _u A _{1u} + A _{2u} + E _g + E _u
(⁴ A _{2g} , ² T _{1g})	(A ₂ , E)	E _u E _g	³ E _u ³ E _g	A _{1g} + A _{2g} + E _g + E _u A _{1u} + A _{2u} + E _g + E _u
	(A ₂ , A ₂)	A _{1g} A _{2u}	³ A _{1g} ³ A _{2u}	A _{2g} + E _u A _{1u} + E _g

Table 3. Selection rules for Cr³⁺ pair transitions in D_{3d} symmetry (S_g = 0, 1).

	³ A _{1g}		³ A _{2u}		³ E _g				³ E _u			
	A _{2g}	E _u	A _{1u}	E _g	A _{1u}	A _{2u}	E _g	E _u	A _{1g}	A _{2g}	E _g	E _u
¹ A _{1g}	A _{1g}	π				σ		π				π
³ A _{1g}	A _{2g}	π	σ		σ			π				π
	E _u	π		σ, π			σ, π		π	π	σ, π	

Table 4. Energies, polarizations and assignments of the ⁴A₂ × ⁴A₂ → ⁴A₂ × ²T₁ observed transitions (T = 9 K).

Energy (cm ⁻¹)	Polarization	Transition
14664	σ, π	¹ A _{1g} → ³ E _g
14654	σ, π	³ A _{1g} → ³ E _g
14535	π	¹ A _{1g} → ³ A _{1g}
14526	π	³ A _{1g} → ³ A _{1g}
14505	π	¹ A _{1g} → ³ E _u

Finally we can estimate *J* = -8 cm⁻¹. The population diagram computed with this value is given in figure 5. It confirms our assumptions of a weak population of levels |2) and |3). Furthermore, absorption spectra at 30 K show a decrease of intensity of transitions from *S* = 0 according to the population diagram for the |0) level.

Up to now we have deduced the exchange parameters only on the basis of the absorption data. A more accurate value for *J* could be deduced from EPR data. Unfortunately since

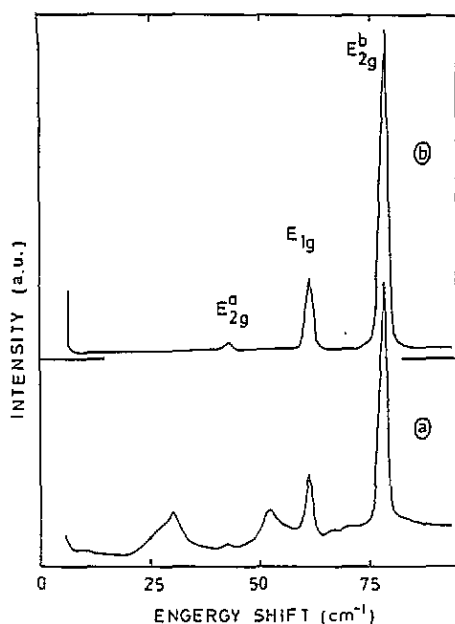


Figure 4. Electronic Raman spectra of $\text{CsCdBr}_3:\text{Cr}^{3+}$ ($T = 4.2$ K). (a) Resonant Raman spectrum (excitation line 514.5 nm). (b) Unpolarized Raman spectrum. The first-order peaks are labelled according to their symmetry (excitation line 457.9 nm).

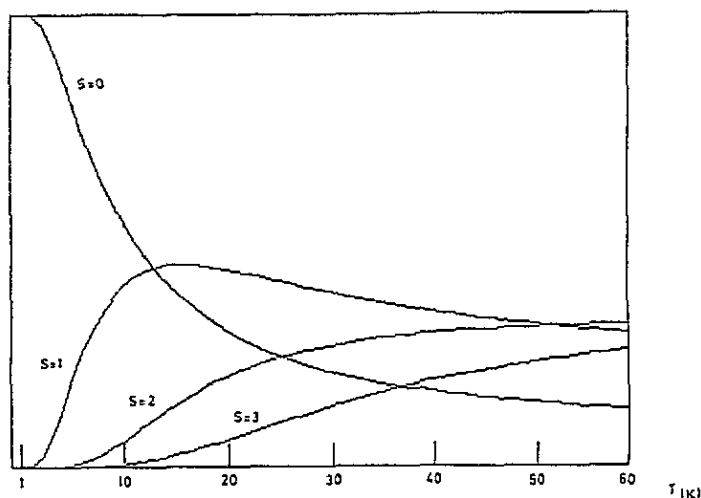


Figure 5. Temperature dependence of the ground state population.

the $\text{Cr}^{3+}-\text{Cr}^{3+}$ pairs are antiferromagnetically coupled, their ground state is $S = 0$ and cannot be observed in EPR spectra. The four resonances arising from the $S = 2$ state and their thermal behaviour are used in fitting the complete energy scheme of the ground state manifold which consists of ten discrete levels. This procedure gives data which differ by an order of magnitude for J , i.e. 15 cm^{-1} (McPherson *et al* 1978) and 1.3 cm^{-1} (McPherson

et al 1979) depending on the fitting approach. In our opinion these figures given for J are to be taken with some care, and in any case, only as limiting values.

The unpolarized Raman spectra of figure 4 give a more direct way to measure the ground state splitting. As previously stated, to a first approximation, the ground state of the ECP consists of four levels with $S = 0, 1, 2, 3$, in order of increasing energy, split by $J, 2J$, and $3J$. If we assign the two bands at 29 and 51 cm^{-1} to the $|0\rangle \rightarrow |2\rangle$ and to the $|0\rangle \rightarrow |3\rangle$ transitions respectively we can calculate from equation (1) $J = 8 \text{ cm}^{-1}$ and $j = 0.4 \text{ cm}^{-1}$. This in turn implies a $|0\rangle \rightarrow |1\rangle$ transition to be observed at about 10 cm^{-1} from the elastic peak. At this energy a shoulder is present but this structure is too weak and too close to the elastic tail to be definitely assigned to the $|0\rangle \rightarrow |1\rangle$ transition.

If we neglect the spin-orbit coupling it is not difficult to calculate the Raman transitions within the ground state and the polarizations. A group theory calculation predicts one $|0\rangle \rightarrow |1\rangle$ transition allowed in zx and zy polarization (taking, as usual, z parallel to the C_3 crystallographic axis), while three lines are expected for both the $|0\rangle \rightarrow |2\rangle$ and $|0\rangle \rightarrow |3\rangle$ transitions (two allowed in zy, zx and one in zz and $(xx + yy)$). In the unpolarized spectrum all these transitions contribute and this could explain on one hand the structured shape of the 29 and 51 cm^{-1} bands, and, on the other hand, the unstructured 10 cm^{-1} peak.

It should be noted that we have assumed the zero-phonon origin of the lines observed in the Raman spectra. We do not believe that they could have a vibronic character. The emission data of the preceding section show that the phonon energy which is mainly coupled to the ECP is of some 140 cm^{-1} higher than the energy in play in the Raman spectra, while it is close to the A_{1g} crystal mode (Pilla *et al* 1987).

This is, to our knowledge, the first time that not only the ground state splitting, but also the fine structure of the spin level has been directly studied. In fact, these features are generally masked both in the emission and the absorption spectra, and their determination has been possible only in the case of Cr^{3+} pairs in high crystal field by means of high resolution emission spectroscopy.

In conclusion, a series of data on the optical spectra of ECP of Cr^{3+} in CsCdBr_3 have been presented. The determination of the exchange parameters has been possible from the direct evidence of the ground state splitting in the resonant Raman spectra. The values we found are in good agreement with the others available on similar systems.

Acknowledgments

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