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To cite this version:

J.C. Rivoal, C. Grisolia, J.P. Torre, M. Vala. Magneto-optical evidence of magnon sidebands in Cs$_3$CoCl$_5$. Journal de Physique, 1985, 46 (10), pp.1709-1716. 10.1051/jphys:0198500460100170900 . jpa-00210121

HAL Id: jpa-00210121
https://hal.archives-ouvertes.fr/jpa-00210121
Submitted on 1 Jan 1985

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Magneto-optical evidence of magnon sidebands in Cs₃CoCl₅

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(Reçu le 13 mars 1985, accepté le 7 juin 1985)

Résumé. — Nous effectuons une étude magnétooptique à haute résolution et en utilisant un nouveau type de cryostat optique He₃ de la transition interdite de spin 4A₂ → 2E de Co²⁺ dans Cs₃CoCl₅. Nos résultats expérimentaux étendus jusqu'à une température inférieure à la température d'ordre du cristal (TN = 0.52 K) sont en accord avec ceux précédemment obtenus à plus haute température mais ne peuvent être interprétés en utilisant le modèle de l'ion simple. L'étude détaillée de la variation de l'intensité d'absorption et du dichroisme circulaire magnétique des différentes raies, en fonction de la température (entre 0.8 et 50 fois TN), montre que le mécanisme dipolaire électrique d'échange est à l'origine de la levée d'interdiction de la transition. L'énergie d'échange déduite de nos expériences |J'/k| = 0.11 K est en accord avec la valeur connue J'/k = 0.111 K. La séparation en champ nul de l'état excité 2E est moins de 1 cm⁻¹ au lieu de la valeur 28 cm⁻¹ estimée en utilisant le modèle de l'ion simple.

Abstract. — A magneto-optical study of the spin-forbidden 4A₂ → 2E transition of Cs₃CoCl₅ below its antiferromagnetic ordering temperature (TN = 0.52 K) has been conducted under high resolution conditions using a new type of He³ optical cryostat. Our experimental results are in agreement with those observed previously but cannot be interpreted by using the single ion model. Careful analysis of the temperature variation of both absorption and magnetic circular dichroism spectra, between 0.8 TN and 50 TN, leads to the conclusion that the spin forbiddeness is removed via an exchange induced electric dipole mechanism. The experimentally deduced exchange energy |J'/k| = 0.11 K is in agreement with the known value J'/k = 0.111 K and the zero field splitting of the 2E state is less than 1 cm⁻¹ instead of the 28 cm⁻¹ value deduced from the single ion model.

1. Introduction.

Over the last twenty years crystalline Cs₃CoCl₅, which contains nearly tetrahedral CoCl₂⁻ units [1, 2], has been the subject of numerous spectroscopic studies including ESR [3, 4], UV-visible absorption [5, 6], polarized vibrational and Raman spectra [7], Zeeman effect [8, 9], pressure studies [10] and magnetic circular dichroism [11]. These results were first analysed in terms of a crystal field model [12, 13]. Later on Bird et al. gave a complete assignment of the forbidden transitions observed via a molecular orbital description which included the effects of spin-orbit coupling and vibrational interaction [6].

Except for the ESR work, none of the previous studies accounted for the possible magnetic exchange between the Co²⁺ ions. Since the Néel temperature is very low (TN = 0.52 K [1, 4]), the magnetic exchange interaction in this 3D-compound was expected to be very small and its effect on the spectra not significant. However, two recent studies have led us to question this supposition. The first, a study of the spin density and bonding of the CoCl₂⁻ ion in Cs₃CoCl₅ [15] by polarized neutron diffraction, concluded that the spin density exhibits distinct noncubic symmetry which may arise from longer-range « crystal » effects far from the CoCl₂⁻ ion. And in the second, we determined the magnetic ordering and we confirmed the magnetic structure of the parent crystal Cs₃MnCl₅ and showed that the forbiddeness of the optical transitions was removed even above the ordering temperature by an exchange-induced dipole mechanism [16].

Since both the Co and Mn crystals have the same crystallographic and magnetic structure and, in addition, order antiferromagnetically at about the same Néel temperature, we decided to investigate in detail the most often studied optical transition in crystalline Cs₃CoCl₅ in order to clarify the mechanism responsible for the lifting of its electric dipole forbiddeness.

In § 2 we summarize the previous work on the
subject with the $^4A_1 \rightarrow ^2E$ transition used as an example. We then describe the experimental set-up in § 3, and give our magnetooptical results in § 4. In § 5 we discuss these results and show that the exchange mechanism is responsible for the intensity borrowing in the observed transitions.

2. Summary of previous work.

Cs$_3$CoCl$_5$ crystallizes in the D$_{4h}^{18}$ space group. Each Co$^{2+}$ ion is surrounded by four chlorine ions which form an almost perfect tetrahedral environment (with a small elongation along the optical axis [2]). The tetrahedral crystal field splits the sevenfold-degenerate ground state ($L = 3$) of the Co$^{2+}$ ion into two orbital triplets and one orbital singlet with the singlet lying lowest. The spin degeneracy is fourfold leading to a $^4A_2$ ground state. The combination of spin-orbit coupling and an axial crystal field splits the ground state into two doublets (E' and E" in D$_{2d}$ symmetry) separated by 8.6 cm$^{-1}$ [17]. Although ESR spectroscopy [4] located these two doublets with less accuracy than the optical study, it allowed the determination of the sign of the zero field splitting: the $\pm 3/2$ doublet (E') lies below the $\pm 1/2$ (E") doublet. This result was also obtained theoretically by Feneuille and Pelletier-Allard [18].

Magnetic Co$^{2+}$ ions form a simple tetragonal lattice with a c/a ratio of about 1.1 so that the structure is approximately cubic. The caloric data are in better agreement with a b.c.c. than an s.c. structure. The existence of a static crystal field which splits the $^4A_2$ ground state leads to an Ising system [19]. The antiferromagnetic ordering occurs at $T_N = 0.52$ K. From ESR measurements in Co$^{2+}$/Cs$_3$ZnCl$_5$, Van Stapele et al. [20] found that the exchange within the a-a plane is antiferromagnetic whereas the interaction along the c axis is ferromagnetic but about 25% smaller in magnitude. The exchange constant was evaluated [19] on the basis of a proposed magnetic structure of 4 antiparallel and two parallel nearest neighbours. Its value is $J'/k = -0.111$ K.

If we exclude the intense $^4A_2 \rightarrow ^4T_1$ (P) transition located between 600 and 700 nm, which gives the blue colour of the crystal, all the observed transitions in the UV-visible range are spin-doublets and consequently are all forbidden. They can gain intensity by second order mixing with quartet states via spin-orbit coupling. This approach was used by us previously [21]. In this respect, we disagree with some of the previous results [22] (vide-infra). Considering that the same mechanism removes the forbiddenness of the transitions, Bird et al. [6] assigned all the doublet states using and testing a molecular orbital description of the ligand field spectra. In their study of the $^4A_2 \rightarrow ^2E$ transition they noted an anomalous temperature variation in the intensities of the lines. This fact was also noted by Pelletier-Allard who attributed the variation to a phase transi-

3. Experimental.

3.1 Apparatus. — The experimental set-up for absorption and MCD experiments has been described previously [23]. The two spectra are taken successively under the same optical conditions. A homemade high resolution monochromator was used with a spectral bandwidth of $\Delta \sigma = 0.6$ cm$^{-1}$ in the 26 000 cm$^{-1}$ region. To avoid mechanical backlash in successive scans, we monitored the change in wavenumber by using an optical scanner (General Scanning Inc.) as suggested to us by Day [24]. Using a silicon refractor plate of 3.4 cm thickness, we are able to change the spectral energy by about 50 cm$^{-1}$ with a linearity of about 1%. The modulation of the polarized light was carried out using a new photoelastic modulator [25] which is particularly free of static birefringence.

To get our low temperature spectra, we used an optical cryostat (Fig. 1) derived from the device of Chanin and Torre [26]. The internal hermetically-sealed gas-handling He$_3$ system and activated charcoal adsorption pump are located inside a super-

Fig. 1. — Schematic of the optical He$_3$ cryostat.
insulated He⁴ cryostat. When the valve V is closed and the He⁴ bath pumped below 2 K, the well isolated evaporating chamber (E) heats up the He³ gas to about 10 K, increasing the pressure inside the whole He³ cryostat. The He³ gas starts to condense in the connecting tube between R and E and drops into the evaporating chamber. A rod passing through the neck of the cryostat is used to open the valve V putting the cryopump into the circuit and cooling the He³ bath to its operating temperature. The lowest temperature reached by the sample was 0.4 K, but the temperature in the evaporator has been checked to be close to 0.3 K. For the magneto-optical experiments, the cryostat was placed in an electromagnet capable of a maximum field of 0.7 T with an air-gap of 2.7 cm.

3.2 CRYSTALS. — Crystals were obtained by slow evaporation of an aqueous solution of CoCl₂ containing at least four moles of excess CsCl. Since the crystals are uniaxial, they were oriented using a polarizing microscope and polished by standard techniques. Typically, the thickness of the crystals studied was 0.3 to 0.5 mm.

In an earlier stage of this study we used crystals prepared by Nerozzi and Briat in our lab using the Bridgman method. Although the chemical analysis of these crystals was identical to that of those crystals obtained in solution, their optical spectra were very different. A comparison of the spectra led us to the conclusion that in the latter case, there were several crystallographic sites despite the fact that X-ray Laue photographs showed no differences.

4. Magneto-optical spectra of the \( {^4\text{A}_2} \rightarrow {^2\text{E}} \) transition.

Of all the quartet to doublet transitions observed in the UV-visible spectrum, the \( {^4\text{A}_2} \rightarrow {^2\text{E}} \) transition is well separated from its neighbours and has been extensively studied. The spectrum consists of a progression in the totally symmetric mode (\( \text{a}_1 \)) with other modes superimposed on it. We will restrict our attention to the first 50 cm⁻¹ of the spectrum considered in previous studies to be the region of the electronic origin lines.

All the previous experimental work [1-14] concluded that the ground state is comprised of two levels. The \( {^4\text{A}_2} \) ground state of the Co²⁺ ion in a tetrahedral environment is split under the action of a tetragonal distortion and spin-orbit coupling into two levels separated by \( E_0 = 8.6 \text{ cm}^{-1} \). We label these levels \( \pm 3/2 \) for the lowest and \( \pm 1/2 \) for the highest following the ESR results [4]. Whether the \( {^2\text{E}} \) excited state is split by S. O. [11] or by vibronic coupling has been extensively discussed [14]. Applying a magnetic field along the \( c \) axis of the crystal lowers the site symmetry from \( D_{4h} \) to \( S_4 \) in which allowed transitions are of the \( \pi, \sigma_+ \) or \( \sigma_- \) nature (Fig. 5). Magnetic circular dichroism (MCD) which measures the difference in absorbance for \( \sigma_+ \) and \( \sigma_- \) polarizations \( (\Delta \alpha = \alpha_{\sigma_+} - \alpha_{\sigma_-}) \) is well suited to check the selection rules established using previous models [27].

4.1 ABSORPTION. — The axial spectrum is shown in figure 2 at 4.2 K and 0.44 K the lowest temperature reached. The observed bands are labelled a, b, c and d according to reference [11] and \( U_1, U_2, U_3, U_4 \) according to reference [14]. We will use the former notation for our discussion.

Band c is not seen in the axial spectrum since it is only \( \pi \) polarized. Its temperature variation was followed and it was noted that the band disappears below 1.3 K. With the high resolution used in our experiments band d appears to be at least a doublet. On its high energy side a number of overlapping bands appear.

Bands a and b are well isolated below 10 K, their shapes are symmetrical, but only b retains intensity below 1.3 K. Clearly the a and c bands are « hot » bands.

The temperature variation of the a and b bands above liquid helium temperature is shown in figure 3 at an enlarged scale. Their intensities decrease while that of band d increases when temperature decreases.

To follow these intensity variations in a quantitative way, we determined the zero order moments of the b and d bands. Since the absorbance \( (\alpha) \) of band b becomes a constant \( (\alpha_0) \) below 1.3 K we give (Fig. 4a) the temperature variation of \( \alpha - \alpha_0 \) versus \( T \) on a log-log scale. A linear variation is seen with slope 2.2.

The area of band \( d \) is more difficult to estimate since it overlaps with higher energy bands. The spectrum was truncated at 26 375 cm⁻¹ for the moment calculation because at this point the intensity is almost constant and independent of the temperature.

The area of band d is shown in figure 4b. It is seen to follow a \( 1/(1 + \exp - E_0/kT) \) law with \( E_0 \approx 8.6 \text{ cm}^{-1} \), in agreement with the Boltzmann population of the ground state of a two level system.

At the lowest temperature (0.44 K) only band b has nonzero intensity in the \( \pi \) spectrum (not shown here). That intensity is the same as the intensity of the axial and \( \sigma \) spectra of this band within 10 % experimental error.

4.2 MAGNETIC CIRCULAR DICHROISM. — The MCD spectra at two different temperatures, taken with a low field \( B = 0.05 \text{ T} \), applied along the direction of propagation of the light is shown in figure 2b. Above 0.1 T the lines broaden because the Zeeman splitting induced becomes of the order of magnitude of the width of the lines.

Bands a and b are S shaped with the same sign, while band d as a complex structure. By lowering the temperature band a vanishes as the corresponding absorption. In band b the positive part, corresponding to a \( \sigma_+ \) transition, also vanishes, while the negative part remains almost constant.
Fig. 2. — Absorption and MCD spectra of the origin region of the $^4A_2 \rightarrow ^2E$ transition. a) Absorption at $T = 4.16$ K (full line) and $T = 0.44$ K (dotted line). b) MCD at $T = 4.5$ K (full line) and $T = 0.48$ K (dotted line) under an external applied field $B = 0.05$ T.

The ratio of the zero order moment of the MCD ($\langle \Delta A \rangle_0$) to the zero order moment of the absorption ($\langle A \rangle_0$) for the b band was determined and is shown in figure 6. The experimental points can be fit with a hyperbolic tangent law:

$$\frac{\langle \Delta A \rangle_0}{\langle A \rangle_0} = K \tanh \frac{3 g \mu_B B}{2 kT}$$

where $K$ is a constant ($K = -2$ in this case), $g$ the Landé factor of the ground state, $\mu_B$ the Bohr magneton, $k$ the Boltzmann constant and $B$ the applied magnetic field. Using this expression and the results of figure 6, we find $g = 17.5$ instead of the value $g = 2.3$ deduced from the ESR results [4]. This result raises a question since Harada et al. [9e] fit their observed Zeeman splitting using a value of $g = 2.43$. In this respect it is important to note

5. Discussion.

Since the single ion model has been used in previous studies, we first compare our experimental absorption and MCD results to this model and show that it is unapplicable. Then we show that including the exchange coupling between Co$^{2+}$ ion leads to good agreement between experiment and theory.

5.1 Single Ion Model. — Relative intensities of the polarized transitions, derived using perturbation theory are given in figure 5. The Zeeman scheme is taken from reference [11] but we note that the $\pi$ transition from the $| ^4A_2 \pm 3/2 \rangle$ ground state cancels out if we take into account both the $| ^4T_1 U_{3/2} \rangle$ and $| ^4T_1 U_{5/2} \rangle$ contributions to the $| ^2E U' \rangle$ excited state [27].

In this model the temperature variations of the bands are assumed to follow the Boltzmann population of the $\pm 1/2$ and $\pm 3/2$ ground levels. Bands a and c (resp. b and d) must decrease (resp. increase) when the temperature decreases. The intensity of band a follows qualitatively the expected variation and disappears at 1.3 K (Fig. 2). The c band also disappears at the lowest temperature. It can be concluded that both a and c bands start from the $\pm 1/2$ level. The temperature variation of the d band follows the Boltzmann population of the $\pm 3/2$ ground level (Fig. 4b), but the temperature variation of the b band does not. As seen in figure 3, above 10 K both the intensity and width of a and b bands are quite similar. Below 10 K the intensity of the a band starts to decrease more rapidly when the temperature is lowered.

Using the single ion model depicted in figure 5 it is impossible to explain (i) the non zero $\pi$ intensity of band b, (ii) the decrease in intensity of band b, and (iii) the narrowing of both a and b bands in the $\pi$ spectrum. This narrowing clearly indicates that the a and b bands are multiple in nature and are not single electronic lines. The zero order moment of the b band (Fig. 4a) follows an $\alpha T^2 + A_0$ variation which cannot be accounted for by the single ion model.

Turning to the MCD results, we expect for a doublet ($\pm 3/2$ in the ground state) to doublet ($\pm 3/2$ in the excited state) that the ratio of the zero order moment of the MCD to the zero order moment of the absorption should vary as the population of the ground state. Namely:

$$\frac{\langle \Delta A \rangle_0}{\langle A \rangle_0} = K \tanh \frac{3 g \mu_B B}{2 kT}$$

Fig. 3. — Temperature variation of the absorption of bands a, b and d at $T = 25.7$ K (-----), $T = 11.3$ K (-----) and $T = 5.6$ K (-----).
that the Zeeman splitting is only observed using an external field greater than 1 tesla. We will discuss this discrepancy below but it is worth noting that more than other experiments our MCD results contradict the single ion model since the observed amplitude (K factor) is too low by more than one order of magnitude.

5.2 Exchange Coupling between \( {\text{Co}}^{2+} \) Ions. —

The Hamiltonian used so far, in zero magnetic field takes into account the distorted tetrahedral crystal field and the spin-orbit coupling of the \( {\text{Co}}^{2+} \) ion. Having in mind the results obtained on the parent crystal \( \text{Cs}_3\text{MnCl}_5 \) [16] we shall now investigate the effect of an exchange field between \( {\text{Co}}^{2+} \) ions. Because \( \text{Cs}_3\text{CoCl}_5 \) orders antiferromagnetically at \( T_N = 0.52 \text{ K} \) [19] the effect of this exchange field, on the energy levels deduced in the single ion model, is expected to be small. Also, the magnon dispersion will be restricted to at most one wavenumber. However as Tanabe has shown [28], the magnetic exchange can be the dominant mechanism of intensity borrowing, even above the ordering temperature.

Below \( T_N \) the cobalt ions arrange themselves in two interpenetrating sublattices having their spins antiparallel. The magnetic unit cell is simple cubic or body centred cubic [19]. This crystal has been considered as an ideal Ising system because its \( \pm 3/2 \) ground state is well isolated when \( kT \ll E_0 \) [29].
Using the standard Ising Hamiltonian [19]:

\[ \mathcal{H}_{\text{ech}} = - \frac{J'}{2S} \sum_i S_i^+ S_i^- \] for \( S = 1/2 \)

the energy levels for this antiferromagnetic system can be calculated in this model (Fig. 7).

The electric dipole moment operator acts only on the orbital part of ground and excited states. Since the ground state in octahedral symmetry is a spin quartet (\( S = 3/2 \)) and the excited state a spin doublet (\( S' = 1/2 \)) the process giving rise to an electronic transition must ensure that the total spin angular momentum is conserved. As proposed by Tanabe et al. [28] this can be done by simultaneous excitation of one exciton in the up (resp. down) sublattice and at least one magnon in the down (resp. up) sublattice. For an excitation in the up sublattice between, for example, \( m_e = + 3/2(A_2) \) and \( m_m = + 1/2(2E) \) corresponding to \( \Delta m_e = - 1 \), there are three possible ways to get \( \Delta m_m = 0 \). The first and second (labelled 1 and 2 in Fig. 7) create a magnon between the \(- 3/2 \) and \(- 1/2 \) or \(- 1/2 \) and \(+ 1/2 \) ground sublevels. The third one (3 in Fig. 7) annihilates a magnon between the \(+ 1/2 \) and \(+ 3/2 \) ground sublevels in the down sublattice. With such a simple picture it is seen that the intensity of an exciton magnon line will depend on the population of ground sublevels. If \( kT \) is greater than \( E_0 \), magnons associated with 1, 2 and 3 transitions will be thermally populated (Fig. 7). But only transition 1 will remain at \( T = 0 \) K. Thus the usual combination of « hot » and « cold » exciton-magnon combinations is somewhat more complicated. There are two « hot » for only one « cold » exciton-magnon combination. Then, for \( kT > E_0 \) the absorption intensity will come mainly from the « hot » combinations, as in the case of ferromagnetic crystals. In this respect the experimental variation in the intensity of the b band can be correlated with the predicted \( T^2 \) variation law of the intensity of exciton-magnon combination absorption lines in the ferromagnetic NiBr₂ having an orbital singlet ground state [31].

The saturation effect observed on the MCD of band b, when \( kT \) is lower than \( E_0 \), can also be explained with the same model. The MCD of an exciton-magnon combination line is expected to be zero because when we create a \( \sigma_+ \) transition exciting an exciton in the up sublattice and a magnon in the down sublattice we also create a \( \sigma_- \) transition exciting an exciton in the down sublattice and a magnon in the up sublattice and both appear at the same energy if the Landé factors of the ground and the excited state are the same. But, if the Landé factors are different we observe an MCD \( S \) shaped term, because \( \sigma_+ \) and \( \sigma_- \) transitions do not appear at the same energy. However, because of the low field used in our experiments, the Zeeman displacements of the levels are small and the splitting between \( \pm 3/2 \) ground levels in the up sublattice can be written:

\[ W = \Delta - g \mu_B B \]

If we suppose that the transition issuing from the \(- 3/2 \) ground level (Fig. 7) is \( \sigma_+ \) polarized, the transition issuing from the \(+ 3/2 \) level will be \( \sigma_- \) polarized using the time reversal theorem. Then the hyperbolic tangent variation of \( \langle \Delta A \rangle_0 / \langle A \rangle_0 \) will come from the Boltzmann population of the \( \pm 3/2 \) levels under applied field

\[ \langle \Delta A \rangle_0 / \langle A \rangle_0 \sim \tanh \frac{W}{2kT} \]

leading to a value of \( | J'/k | = 0.11 \) K in good agreement with the known value \( J'_\| / k = -0.111 \) K [19]. These experimental facts provide evidence of the exciton-magnon nature of band b. It is worthy of note that the results cover the entire range from below to far above the ordering temperature but with only the zero vibrational ground state populated. Moreover, the fact that the absorption intensity of band b has an isotropic behaviour at very low temperature (cf § 4a) is in agreement with the model. Since the Co²⁺ ions form a cubic structure, an isotropic exchange interaction between them leads to an intensity of the exciton-magnon combination absorption band which is isotropic. The a band can also be attributed to an exciton-magnon combination on the basis of the close parallelism of its absorption and MCD spectra to those of band b (cf. Fig. 2).

5.3 VIBRATIONAL COUPLING. — The nature of the d band and the related components on its high energy side (Fig. 2) is different. Their absorption intensities follow simply the Boltzmann law for a two level transitions.

![Fig. 7. — Zeeman diagram of the \(^4A_2 \rightarrow \^2E\) transition with an antiferromagnetic exchange field leading to two interpenetrating sublattices (up and down). The arrows indicate the exciton-magnon transitions.](image-url)
ground state. Bands d and b were claimed [11] to be electronic transitions between the same ground state and the spin-orbit split components of the $^2E$ state. It is clear from figure 3 that this assumption is incorrect. Since we know the vibrational lattice energy of Cs$_3$CoC$_15$ in the ground state [7] and assuming that it is of the same order of magnitude for the excited state, we can see that band d correlates well with the lowest vibrational energy of the lattice. We then attribute band d and higher energy components to exciton-phonon bands which intensities are expected to follow a Boltzmann law [32]. Whether or not a pseudo Jahn-Teller effect is at the origin of the structure is beyond the scope of this work. But the analysis of Harada et al. [14] has to be reviewed since they also assumed that the d band was the spin-orbit split component of the $^2E$ state.

5.4 SPIN-ORBIT COUPLING IN THE EXCITED STATE. — The first order perturbation treatment leads to a null splitting of an orbital E state under spin-orbit coupling [21]. Second-order perturbation between $T_1$ and $T_2$ states and E can induce a splitting, but it is expected to be small. Our previous estimation of such a splitting in the case of Cs$_3$MnC$_15$ [16] was of few wavenumber. In Cs$_3$CoC$_15$ the $^2E$ state is well isolated from its neighbours by at least 2 000 cm$^{-1}$, so the splitting is expected to be smaller than in the manganese case. Our previous analysis leads us to assign the d band to a vibrational excited state, and the a and b bands to the same excited state. This single excited state is then the $^2E$ state and the s.o. splitting in that state is lower than the bandwidth ($\approx 1$ cm$^{-1}$ half-width). This result is in agreement with previous calculations but again contradicts the assignment made with the single ion model.

6. Conclusion.

All our results described above corroborate the previous experiments [1-14], but are interpreted using a completely different model. Using a high resolution spectrophotometer and a new type of He$^3$ cryostat, we have measured the absorption and magnetic circular dichroism spectra of the $^4A_2 \rightarrow ^2E$ spin forbidden transition of crystalline Cs$_3$CoC$_15$ above and below its antiferromagnetic ordering temperature. The temperature dependence of the various absorption bands and their associated MCD under a low magnetic field, in the range 30 K-0.44 K has allowed us to study the electronic transitions starting from the zero order vibrational ground state. The in-depth analysis of our magneto-optical experiments have led us to the following conclusions:

i) The lifting of the spin-forbiddenness of the $^4A_2 \rightarrow ^2E$ transition is achieved by an exchange induced mechanism even above $T_N$ instead of the spin-orbit coupling mechanism proposed previously.

ii) The spin-orbit coupling of the $^2E$ excited state is less than $1$ cm$^{-1}$ instead of 28 cm$^{-1}$ as proposed previously.

The ground state of the absorbing centres is well described by considering a splitting of the $^4A_2$ cubic ground state of an individual Co$^{2+}$ ion — into two Kramers doublets split by 8.6 cm$^{-1}$ under spin-orbit coupling and tetragonal distortion — and the antiferromagnetic interaction between magnetic ions leading to a further splitting of each doublet. The splitting of the $\pm 3/2$ ground doublet is close to 1 cm$^{-1}$.

We now believe that all the spin-forbidden transitions of Cs$_3$CoC$_15$ observed in the UV-visible range need to be reinvestigated by considering the mechanism used here and originally proposed by Tanabe et al. [28].

Acknowledgments.

The authors are grateful to P. Bassoul who kindly provided us with the X-ray Laue diagrams of the different crystals used in this study. We gratefully acknowledge O. Lucas and M. Planchais in an earlier stage of this study and M. Le Liboux and R. Nahoum for technical assistance. We are indebted to N. Bon-temps and B. Briat for criticism of our manuscript. Thanks are also due to the NATO organization for partial support of this research.

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