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# STRESS INDUCED LINEAR DICHROISM OF ANTIFERROMAGNETIC PEROVSKITES : KNiF<sub>3</sub>, KCoF<sub>3</sub> AND RbCoF<sub>3</sub>

## II. — SPECTROSCOPIC CALCULATIONS AND ASSIGNMENTS

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**Résumé.** — Dans l'article précédent, nous avons démontré que dans les matériaux ordonnés magnétiquement, le dichroïsme linéaire (DL) sous contrainte a une origine magnétique. Nous présentons ici le calcul de ce DL pour des transitions d-d dans KNiF<sub>3</sub>, KCoF<sub>3</sub> et RbCoF<sub>3</sub>. Les spectres de DL correspondants sont comparés aux spectres de dichroïsme linéaire magnétique (DLM) des composés dilués Ni<sup>2+</sup>/KZnF<sub>3</sub>, Co<sup>2+</sup>/KMgF<sub>3</sub>. Dans KNiF<sub>3</sub> nous avons calculé le DL sous contrainte en-dessous de  $T_N$ , c'est-à-dire le DL dû à un domaine dont les spins sont orientés le long de la contrainte ( $S \parallel \langle 001 \rangle$ ). Pour les transitions excitoniques pures et exciton-phonon, ce DL est égal au DLM de composés paramagnétiques. Pour le Co<sup>2+</sup>, les transitions de Co<sup>2+</sup>/KMgF<sub>3</sub> ne présentent pas de DLM. Le DL sous contrainte que nous observons dans KCoF<sub>3</sub> à  $T < T_N$  est lié au fait que l'interaction d'échange est du même ordre de grandeur que l'interaction spin-orbite. L'accord entre nos calculs et les spectres expérimentaux nous permet d'attribuer plusieurs termes spectraux et composantes spin-orbite dans KNiF<sub>3</sub>. Nous pouvons aussi conclure qu'il y a cohérence entre nos résultats et deux hypothèses que nous avions faites pour les matériaux magnétiques : les phonons à  $k = 0$  sont les plus actifs dans le spectre optique et l'interaction d'échange est faible dans les états excités.

**Abstract.** — We have demonstrated in the preceding article that the linear dichroism (LD) under stress in magnetically ordered compounds has a magnetic origin. Here we present the calculation of this LD for d-d transitions in KNiF<sub>3</sub>, KCoF<sub>3</sub>, RbCoF<sub>3</sub>. We compare the corresponding LD spectra to the magnetic linear dichroism (MLD) spectra of diluted compounds : Ni<sup>2+</sup>/KZnF<sub>3</sub>, Co<sup>2+</sup>/KMgF<sub>3</sub>. In KNiF<sub>3</sub>, the LD under a  $\langle 001 \rangle$  stress, below  $T_N$ , is the LD given by a domain whose spins lie along the  $\langle 001 \rangle$  direction. We have calculated it for exciton and exciton-phonon bands by applying the formula of the MLD for paramagnetic compounds to stressed magnetic crystals. The transitions of Co<sup>2+</sup>/KMgF<sub>3</sub> give no MLD. The LD under stress in KCoF<sub>3</sub> for  $T < T_N$  is related to the fact that the exchange and the spin-orbit interactions are of the same order of magnitude. The agreement between our calculations and the experimental spectra allows us to assign several spectral terms and spin-orbit components in KNiF<sub>3</sub>. We can also conclude that our results are consistent with two hypotheses we made about the magnetic materials : the  $k = 0$  phonons are the most efficient in the absorption spectra and the exchange interaction in the excited states is weak.

**1. Introduction.** — In previous papers we have shown, for KNiF<sub>3</sub>, KCoF<sub>3</sub> and RbCoF<sub>3</sub>, that the linear dichroism (LD) induced by a stress below  $T_N$  has a pure magnetic origin [1-3], i.e., it is due to the difference in the interaction of light polarized parallel and perpendicular to the magnetization of the sublattices. In this paper we shall confirm this point by considering spectroscopic arguments. In order to

support our conclusion for KNiF<sub>3</sub>, KCoF<sub>3</sub> and RbCoF<sub>3</sub> we have carried out magnetic linear dichroism (MLD) experiments on corresponding dilute paramagnetic crystals : Ni<sup>2+</sup>/KZnF<sub>3</sub> and Co<sup>2+</sup>/KMgF<sub>3</sub>. We compare the LD under stress in the magnetically ordered materials to the MLD in the dilute compounds. We define the LD by  $\Delta A = A_{\parallel} - A_{\perp}$ . We recall that  $A = \log I_0/I$  where  $I_0$  and  $I$  stand for the incident and transmitted flux. The absorbance  $A_{\parallel}$  ( $A_{\perp}$ ) refers to the light whose electric field vector is polarised parallel (perpendicular) to the stress

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direction for the magnetic compounds or to the magnetic field orientation for the diluted ones. In our experiments the perturbation is applied along a fourfold axis.

Since the theoretical treatment is not the same for the  $\text{Ni}^{2+}$  and the  $\text{Co}^{2+}$  compounds, we have presented the two cases in two different sections (2 and 3). Our experimental results are given in paragraph 2.1 for  $\text{Ni}^{2+}$  and 3.1 for  $\text{Co}^{2+}$ . Before discussing these results (in § 2.3 and 3.3), we present the LD calculations in paragraphs 2.2 and 3.2.

**2. Nickel compounds.** — **2.1 EXPERIMENTAL RESULTS.** — We have compared the LD under stress in  $\text{KNiF}_3$  to the MLD spectrum in the dilute compound  $\text{Ni}^{2+}/\text{KZnF}_3$  (about 6%  $\text{Ni}^{2+}$  ions) in the spectral range 13 500–25 500  $\text{cm}^{-1}$  (Fig. 1, 2). The high absorbance of the studied  $\text{KNiF}_3$  sample (0.5 mm thick) between 23 300 and 25 500  $\text{cm}^{-1}$  did not allow us to perform LD experiments in this spectral region.

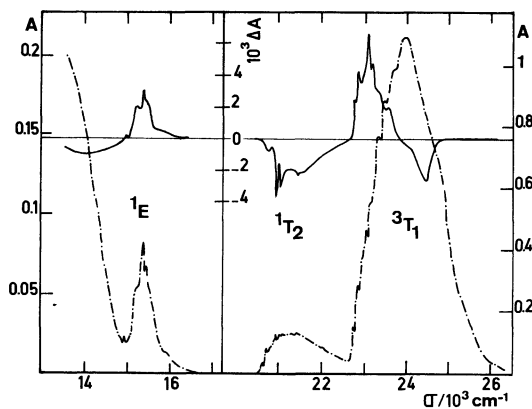


FIG. 1. — Absorption (—) and MLD spectra of  $\text{Ni}^{2+}/\text{KZnF}_3$  at 1.6 K for a 0.7 T magnetic field (bandwidth  $\Delta\sigma = 15 \text{ cm}^{-1}$ ). The sample thickness is 1.95 mm and the concentration in  $\text{Ni}^{2+}$  ions is about 6%.

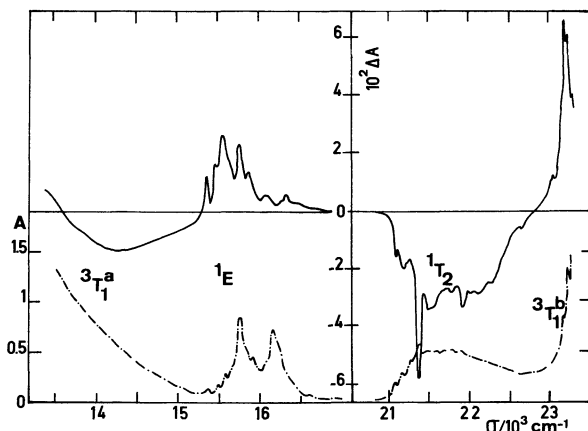


FIG. 2. — Absorption (—) and LD under stress (250  $\text{kgp.cm}^{-2}$ ,  $S // \langle 001 \rangle$ ) spectra of  $\text{KNiF}_3$  at 15 K (bandwidth  $\Delta\sigma = 10 \text{ cm}^{-1}$ ). The sample is 0.5 mm thick.

The LD under stress for  $\text{KNiF}_3$  partly reveals the spin-orbit structure (A, E,  $T_1$ ,  $T_2$  levels) of the spectral terms in an  $O_h$  crystalline field ( ${}^3A_{2g} \rightarrow {}^3T_{1g}^a$ ,  ${}^1T_{2g}$ ,  ${}^3T_{1g}^b$ ,  ${}^1A_{1g}$ ) and the spectrum is very similar to the MLD spectrum obtained for  $\text{Ni}^{2+}/\text{KZnF}_3$  (Fig. 1, 2). Note for  $\text{KNiF}_3$  that the exciton-phonon-magnon band at 16 158  $\text{cm}^{-1}$  does not give any LD. We have mentioned this fact in reference [4].

In low magnetic fields ( $< 0.3 \text{ T}$ ), we have verified that the amplitude of the dichroism on all vibronic bands varies as  $1/T^2$  at low temperature

$$(1.6 < T < 2 \text{ K})$$

for  $\text{Ni}^{2+}/\text{KZnF}_3$  and approximately as the square of the sublattice magnetization for  $\text{KNiF}_3$ .

**2.2 THEORETICAL PREDICTIONS.** — **2.2.1 Absorption process.** — In the spectral range considered here the dipole strengths of the main absorption lines for  $\text{Ni}^{2+}/\text{KZnF}_3$  and  $\text{KNiF}_3$  are very similar [5]. This indicates that the involved transitions  ${}^3A_{2g} \rightarrow {}^3T_{1g}^a$ ,  ${}^1T_{2g}$ ,  ${}^3T_{1g}^b$  for  $\text{KNiF}_3$  are mainly due to a single ion process. In order to explain the origin of the birefringence, we cannot follow Jahn [6] who assumes that exchange dipole transitions of pairs of ions are responsible of the birefringence in the antiferromagnetic iron-group difluorides. For  $\text{KNiF}_3$ , the pair absorption process is an exception : only one exciton-photon-magnon band for the transition  ${}^3A_{2g} \rightarrow {}^1E_g$  [4] and double excitonic transitions in the ultraviolet clearly appear as pair transitions.

The intensity of the spin-allowed transitions is mainly due to the presence of odd parity lattice vibrations which mix the even parity levels studied to odd parity levels located in the near ultraviolet [7, 8]. The spin forbidden transitions then take their intensity from the spin allowed one by spin-orbit interaction.

For magnetic dipole (zero-phonon) transitions we have verified that we obtain similar oscillator strengths in  $\text{Ni}^{2+}/\text{KZnF}_3$  and in  $\text{KNiF}_3$ , which agrees with theoretical predictions [9]. Moreover, the corresponding oscillator strengths are close to those reported in reference [8].

We have also verified that the absorption and the magnetic circular dichroism (MCD) of  $\text{Ni}^{2+}/\text{KZnF}_3$  for vibronic bands in the studied spectral range, are proportional to the  $\text{Ni}^{2+}$  concentration (between  $2 \times 10^{-3}$  and  $6 \times 10^{-2}$ ). From this we conclude that pairs, triads... of  $\text{Ni}^{2+}$  ions do not influence optical and magneto-optical measurements in the more concentrated crystal. Thus MLD calculations need only be carried out for single ion transitions.

**2.2.2 MLD calculations for  $\text{Ni}^{2+}/\text{KZnF}_3$ .** — In the MLD formula which is deduced in the rigid shift approximation, the term proportional to the shape function of the absorption line  $f(\sigma)$ , and related to the ground state population, predominates at low temperature [10]. In this case, for a transition occurring at

temperature  $T$ , under a magnetic field  $H$ , the MLD  $\Delta A$  can be expressed by :

$$\frac{\Delta A}{A_m} = \frac{\Delta A_{m0}}{A_m} \left[ \frac{2[-1 + \cosh(g\mu_B H/kT)]}{1 + 2 \cosh(g\mu_B H/kT)} \right] f(\sigma) \quad (2.1)$$

where  $\mu_B$  is the Bohr magneton and  $g$  the Landé factor of the ground state.  $A_m$  stands for the maximum absorbance of the line in the absence of a magnetic field.

$A_m$  and  $\Delta A_{m0}$  can be written in terms of matrix elements of  $\hat{m}$  ( $\hat{m}$  representing the magnetic or electric dipole moment) between the ground state and the excited state (see appendix A for the general expression for these matrix elements).

For  $\text{Ni}^{2+}$  compounds, if we call  $\Gamma_i$  the spin-orbit components of the  ${}^3\text{T}_{1g}$  excited state, the MLD  $\Delta A$  for the  ${}^3\text{A}_{2g}(\text{T}_2) \rightarrow {}^3\text{T}_{1g}(\Gamma_i)$  transitions can be expressed by formula (2.1).

For the magnetic dipole transition :

$$A_m = \frac{C}{3} \sum_{n,\alpha} |\langle {}^3\text{T}_{1g} \Gamma_i \alpha | \hat{m}_0 | {}^3\text{A}_{2g} \text{T}_2 n \rangle|^2$$

$$\Delta A_{m0} = C \cdot \sum_{\alpha} \left[ \frac{1}{2} |\langle {}^3\text{T}_{1g} \Gamma_i \alpha | \hat{m}_+ | {}^3\text{A}_{2g} \text{T}_2 - 1 \rangle|^2 + \frac{1}{2} |\langle {}^3\text{T}_{1g} \Gamma_i \alpha | \hat{m}_- | {}^3\text{A}_{2g} \text{T}_2 - 1 \rangle|^2 - |\langle {}^3\text{T}_{1g} \Gamma_i \alpha | \hat{m}_0 | {}^3\text{A}_{2g} \text{T}_2 - 1 \rangle|^2 \right].$$

In table I we have reported the calculated  $\Delta A_{m0}/A_m$  values for magnetic dipole (zero phonon) transitions.

TABLEAU I

$\Delta A_{m0}/A_m$  calculated values for magnetic dipole transitions  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\Gamma_i)$ . The  $\Gamma_i$  stand for the spin-orbit components.

$\Gamma_i$	$\text{A}_1$	$\text{T}_1$	$\text{E}$	$\text{T}_2$
$\Delta A_{m0}/A_m$	0	$-\frac{3}{4}$	$\frac{3}{2}$	$-\frac{3}{4}$

We now consider well-separated vibronic transitions in  $\text{Ni}^{2+}/\text{KZnF}_3$ . Their energy suggests that they arise from the interaction between the  $\text{Ni}^{2+}$  ion and the host lattice phonons [5].

We have carried out magnetic circular dichroism (MCD) experiments on the  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}^a$ ,  ${}^1\text{T}_{2g}$ ,  ${}^3\text{T}_{1g}^b$ ,  ${}^1\text{E}_g^a$  transitions of  $\text{Ni}^{2+}/\text{KZnF}_3$ , in order to obtain information about the symmetry of the phonons involved.

Figure 3 shows the MCD spectra for the transitions  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g^a$ ,  ${}^1\text{T}_{2g}$ ,  ${}^3\text{T}_{1g}^b$  for a crystal of  $\text{KZnF}_3$  with a concentration of  $2 \times 10^{-3}$  in  $\text{Ni}^{2+}$  ions.

Following Ferguson *et al.* [5] we have observed the magnetic dipole transition for  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g^a$  at  $14915 \text{ cm}^{-1}$ . The sign of the MCD  $C$ -term (proportional to  $f(\sigma)$ ) on the  $14915 \text{ cm}^{-1}$  line confirms its attribution to the zero-phonon transition. Note that

for the other transitions the strength of the zero-phonon transition is too small to be detected.

The difference in frequency between the magnetic dipole lines and the first more intense vibronic peaks are close to the infrared spectrum frequencies which correspond to transverse optical phonons of symmetry  $\text{T}_{1u}$  at  $\mathbf{k} = 0$  [5, 11]. Moreover we note (Fig. 3) that the three vibronic main lines corresponding to the three  $\text{t}_{1u}$  phonon frequencies present MCD  $C$ -terms and MCD  $A$ -terms (proportional to  $df(\sigma)/d\sigma$ ) of the same sign.

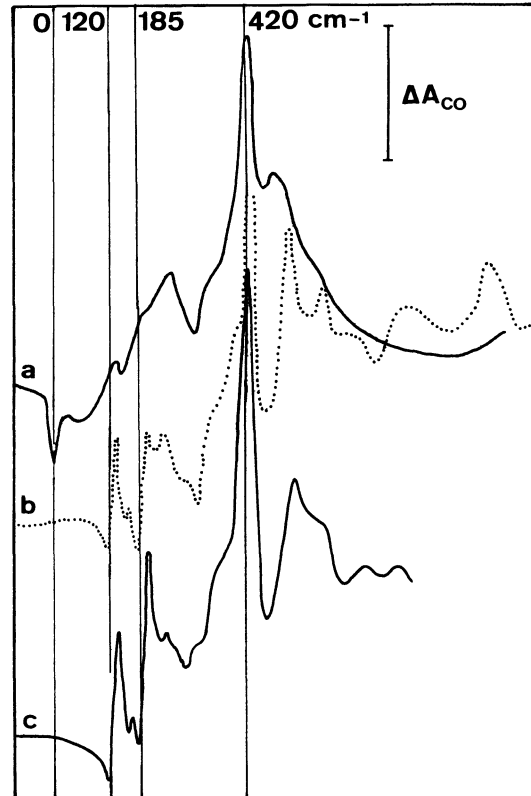


FIG. 3. — MCD spectrum ( $H // \langle 100 \rangle$ , 3.75 T) for  $\text{Ni}^{2+}/\text{KZnF}_3$  at 15 K. a) Transition  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g^a$  (bandwidth  $\Delta\sigma = 4 \text{ cm}^{-1}$ ), unit  $\Delta A_{co} = 2.5 \times 10^{-4}$ . b)  ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}$  ( $\Delta\sigma = 9 \text{ cm}^{-1}$ )  $\Delta A_{co} = 5 \times 10^{-4}$ . c)  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}^b(\text{E})$  ( $\Delta\sigma = 10 \text{ cm}^{-1}$ )  $\Delta A_{co} = 10^{-3}$ . The sample thickness is 8.11 mm and its concentration is about 0.2 %.

We have calculated the electric dipole moments and consequently the MCD terms for well separated vibronic transitions arising from the interaction of the  $\text{Ni}^{2+}$  ions and one phonon of odd parity (see appendix B). The sign and amplitude of the MCD terms depend upon the symmetry of the  $Q_s$  (appendix B) whatever  $\mathbf{k}$  of the phonon is in the Brillouin zone. The calculations are similar to those reported by Harding *et al.* [7].

We can interpret the sign and the amplitude of the experimental MCD terms mainly with  $Q_s = \text{T}_{1u}$ . Since the dispersion with  $\mathbf{k}$  of the transverse optical phonons of symmetry  $\text{T}_{1u}$  at  $\mathbf{k} = 0$  is negligible [11], the  $\mathbf{k} \neq 0$  phonons may give a contribution to the MCD different from that of the  $\mathbf{k} = 0$  phonon of symmetry

$T_{1u}$ . For example, the  $\mathbf{k} \neq 0$  phonons corresponding to  $Q_s = T_{2u}$  should give a contribution of opposite sign. We can then conclude that either the  $\mathbf{k} \neq 0$  phonons corresponding to  $Q_s \neq T_{1u}$  are not involved or the  $\mathbf{k} \neq 0$  phonons do not assist the vibronic transitions [12]. For the first case, we can say, as in [13], that this result arises from the fact that the symmetry  $T_{1u}$  has a particular importance related to the electric field set up by the phonons. One must also determine the nature and the importance of the  $t_{1u}$  contribution to the vibronic spectrum.

In conclusion, in order to calculate the MLD of  $Ni^{2+}/KZnF_3$  we restrict ourselves to  $Q_s = T_{1u}$ , using the formula of appendix B.

We must consider the case of broad vibronic bands which predominate in our spectra. We make the hypothesis that they are assisted by one phonon of odd parity plus phonons of even parity. We then consider the zeroth and first moments of the absorption and of the MLD bands and not simply their amplitude and sign. We use the result of [14] where it is demonstrated that the zero and first moments of the absorption and MLD of broad vibronic bands assisted by phonons of even parity are equal to those of the zero-phonon line. In our case the moments of the broad vibronic bands are equal to those of the transition assisted by only one phonon of odd parity.

By using formula (1) of appendix B, we have calculated the electric dipole operator matrix elements for

spin-orbit components of the  ${}^3A_{2g} \rightarrow {}^3T_{1g}^b$  transition assisted by  $t_{1u}$  or  $t_{2u}$  phonons in  $M_c$  units :

$$M_c = \sum_{T_{2u}} \times \left[ \frac{\langle {}^3T_{1g}^b \| \hat{m} \| {}^3T_{2u} \rangle \langle {}^3T_{2u} \| V_{t_{1u}} \| {}^3A_{2g} \rangle}{W({}^3A_{2g}) - W({}^3T_{2u})} + \frac{\langle {}^3T_{1g}^b \| V_{t_{1u}} \| {}^3T_{2u} \rangle \langle {}^3T_{2u} \| \hat{m} \| {}^3A_{2g} \rangle}{W({}^3T_{1g}) - W({}^3T_{2u})} \right] \times \langle t_{1u} \| Q_{t_{1u}} \| a_{1g} \rangle.$$

The reduced matrix elements written here are deduced from those of appendix B by using the Wigner-Eckart theorem.

Table II gives, as an example, the results for a  $t_{1u}$  vibrational mode. We have shown that the sign of the MLD signal for a given spin-orbit component does not depend on the symmetry  $T_{1u}$  or  $T_{2u}$  of the vibration, in contrast to the sign of the MCD which was opposite for  $t_{1u}$  and  $t_{2u}$  vibration modes.

In the paramagnetic phase the  $\Delta A_{m0}$  and  $A_m$  values (expression (2.1)) for the assisted (by  $t_{1u}$  or  $t_{2u}$  phonons) transition  ${}^3A_{2g} \rightarrow {}^3T_{1g}(\Gamma_i)$  and  ${}^3A_{2g} \rightarrow {}^3T_{2g}(\Gamma'_i)$ , are given in table III in  $CM_c^2$  or  $CM_a^2$  units ( $M_a$  is similar to  $M_c$  for the  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition). Since the intensity of the  ${}^3A_{2g} \rightarrow {}^1E_g^a$  band is mainly due to the mixing of the  ${}^3T_{1g}^b(E)$  state with  ${}^1E_g^a$  by spin orbit coupling, the ratio  $\Delta A_{m0}/A_m$  for  ${}^3A_{2g} \rightarrow {}^1E_g$  is the same as for the  ${}^3A_{2g} \rightarrow {}^3T_{1g}^b(E)$  transition (table III).

TABLE II

Matrix elements of the electric dipole moment (in unit of  $M_c$ ) for the  ${}^3A_{2g}(T_2) \rightarrow {}^3T_{1g}(\Gamma_i)$  transition assisted by  $t_{1u}$  phonons

Transition $T_2 \rightarrow \Gamma_i$	Element	$\beta$	+	-	0
$T_2 \rightarrow A_1$	$\langle A_1   \hat{m}_\beta   T_2 + 1 \rangle$		$-1/\sqrt{6}$	0	$-1/\sqrt{6}$
	$\langle A_1   \hat{m}_\beta   T_2 0 \rangle$		$-1/\sqrt{6}$	$+1/\sqrt{6}$	0
	$\langle A_1   \hat{m}_\beta   T_2 - 1 \rangle$		0	$+1/\sqrt{6}$	$+1/\sqrt{6}$
$T_2 \rightarrow T_1$	$\langle T_1 + 1   \hat{m}_\beta   T_2 + 1 \rangle$		$-1/2$	$+1/2$	0
	$\langle T_1 0   \hat{m}_\beta   T_2 + 1 \rangle$		$+1/2$	0	$+1/2$
	$\langle T_1 + 1   \hat{m}_\beta   T_2 0 \rangle$		0	$+1/2$	$+1/2$
	$\langle T_1 - 1   \hat{m}_\beta   T_2 0 \rangle$		$+1/2$	0	$+1/2$
	$\langle T_1 0   \hat{m}_\beta   T_2 - 1 \rangle$		0	$+1/2$	$+1/2$
	$\langle T_1 - 1   \hat{m}_\beta   T_2 - 1 \rangle$		$+1/2$	$-1/2$	0
$T_2 \rightarrow E$	$\langle E_\theta   \hat{m}_\beta   T_2 + 1 \rangle$		$-1/\sqrt{12}$	0	$-1/\sqrt{12}$
	$\langle E_\epsilon   \hat{m}_\beta   T_2 + 1 \rangle$		0	$1/2$	$1/2$
	$\langle E_\theta   \hat{m}_\beta   T_2 0 \rangle$		$1/\sqrt{3}$	$-1/\sqrt{3}$	0
	$\langle E_\theta   \hat{m}_\beta   T_2 - 1 \rangle$		0	$1/\sqrt{12}$	$1/\sqrt{12}$
	$\langle E_\epsilon   \hat{m}_\beta   T_2 - 1 \rangle$		$-1/2$	0	$-1/2$
$T_2 \rightarrow T_2$	$\langle T_2 0   \hat{m}_\beta   T_2 + 1 \rangle$		0	$+1/2$	$+1/2$
	$\langle T_2 - 1   \hat{m}_\beta   T_2 + 1 \rangle$		$-1/2$	$+1/2$	0
	$\langle T_2 + 1   \hat{m}_\beta   T_2 0 \rangle$		$-1/2$	0	$-1/2$
	$\langle T_2 - 1   \hat{m}_\beta   T_2 0 \rangle$		0	$-1/2$	$-1/2$
	$\langle T_2 + 1   \hat{m}_\beta   T_2 - 1 \rangle$		$+1/2$	$-1/2$	0
	$\langle T_2 0   \hat{m}_\beta   T_2 - 1 \rangle$		$+1/2$	0	$+1/2$

TABLE III

*Absorbance and MLD for vibronic  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\Gamma_i)$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\Gamma'_i)$  transitions for a  $t_{1u}$  phonon*

	$\Gamma_i$	$A_1$	$T_1$	E	$T_2$	Unit
	—	—	—	—	—	—
${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$	$A_m$	1/9	1/3	2/9	1/3	$CM_c^2$
	$\Delta A_{m0}$	1/12	— 1/8	1/6	— 1/8	$CM_c^2$
	$\Delta A_{m0}/A_m$	3/4	— 3/8	3/4	— 3/8	
	$\Gamma'_i$	$A_2$	$T_1$	E	$T_2$	Unit
	—	—	—	—	—	—
${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	$A_m$	1/9	1/3	2/9	1/3	$CM_a^2$
	$\Delta A_{m0}$	1/12	— 1/8	1/6	— 1/8	$CM_a^2$
	$\Delta A_{m0}/A_m$	3/4	— 3/8	3/4	— 3/8	

2.2.3 LD under stress for  $\text{KNiF}_3$ . — Here we treat the case of pure excitonic and exciton-phonon transitions which correspond to single-ion excitations in an antiferromagnet.

Without stress we have supposed that  $d_x$ ,  $d_y$  and  $d_z$  domains are of equal importance in a crystal. We can then write the wavefunction  $|G\rangle$  of the ground state of the entire crystal [9] :

$$|G\rangle = A \prod_{n=1}^N |\psi\rangle_{na} \cdot \prod_{m=1}^N |\psi'\rangle_{mb}$$

$n$  and  $m$  refer to the unit cell in the two sublattices  $a$  and  $b$ ,  $A$  is the antisymmetrisation operator. For  $d_z$  domains  $|\psi\rangle = |{}^3\text{A}_2 + 1\rangle$  and  $|\psi'\rangle = |{}^3\text{A}_2 - 1\rangle$  whereas :

$$\frac{1}{2} |{}^3\text{A}_2 + 1\rangle + \frac{\sqrt{2}}{2} |{}^3\text{A}_2 0\rangle + \frac{1}{2} |{}^3\text{A}_2 - 1\rangle$$

and

$$\frac{1}{2} |{}^3\text{A}_2 + 1\rangle - \frac{\sqrt{2}}{2} |{}^3\text{A}_2 0\rangle + \frac{1}{2} |{}^3\text{A}_2 - 1\rangle$$

are appropriate for  $|\psi\rangle$  and  $|\psi'\rangle$  in  $d_x$  or  $d_y$  domains. Taking into account the three kinds of domains, we find that, for pure excitonic transitions, in the absence of a perturbation, the maximum theoretical absorbance value  $A_m$  is the same in the antiferromagnetic or in the paramagnetic phase for each spin-orbit component. This result allows us to make our calculation with one-ion wavefunctions, if we assume that the intersublattice interaction is negligible. We apply this to exciton-phonon transitions by making the following hypothesis. In such a transition, a phonon of wave-vector  $\mathbf{k}$  in the Brillouin zone and an exciton  $-\mathbf{k}$  are involved. By making the hypothesis that only phonons at  $\mathbf{k} = 0$  [4] are efficient, we can evaluate quantitatively the LD under stress for the exciton-phonon as for the exciton transitions using the isolated  $\text{Ni}^{2+}$  ions calculations. In order to experimentally justify our hypothesis of  $\mathbf{k} = 0$  phonons, we show in figure 4 the MCD spectra of  $\text{KNiF}_3$  for the transitions  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g^a$ ,

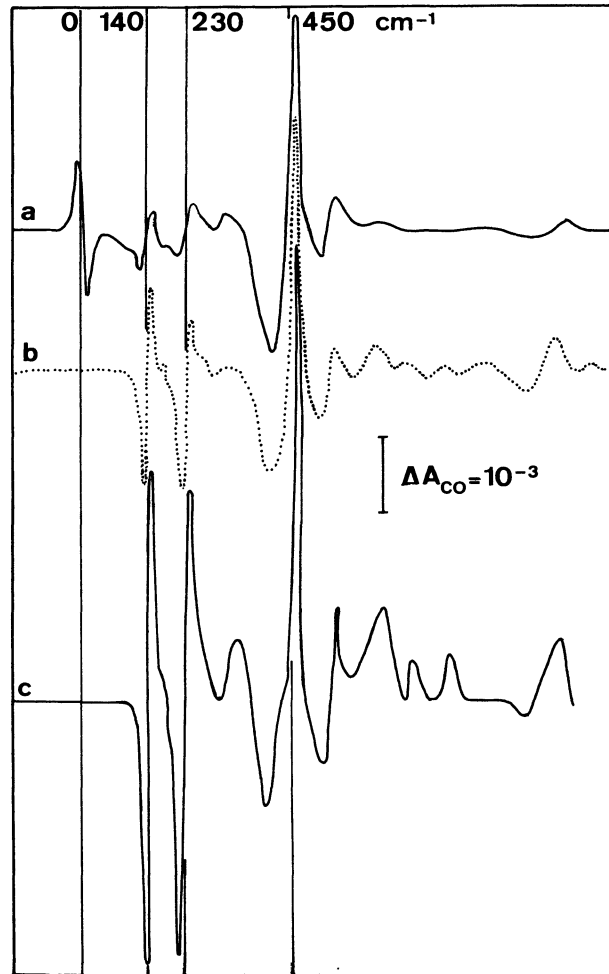


FIG. 4. — MCD spectrum for  $\text{KNiF}_3$  in an antiferromagnetic configuration ( $T = 6.2$  K,  $H \parallel \langle 100 \rangle$ ,  $H = 0.83$  T). a) Transition  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g^a$  (bandwidth  $\Delta\sigma = 2$   $\text{cm}^{-1}$ ). b)  ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}$  ( $\Delta\sigma = 5$   $\text{cm}^{-1}$ ). c)  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{E})$  ( $\Delta\sigma = 5$   $\text{cm}^{-1}$ ). The sample thickness is 0.195 mm.

${}^1\text{T}_{2g}$  and  ${}^3\text{T}_{1g}$  for an antiferromagnetic configuration. We had shown in [4] that the MCD could be interpreted with the transverse optical phonons of symmetry  $t_{1u}$  at  $\mathbf{k} = 0$  for the transition  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g^a$ . This result is also available for  ${}^1\text{T}_{2g}$  and  ${}^3\text{T}_{1g}^b$ .

When a stress is applied we have no longer three

kinds of domains responsible for the isotropy of the radiation in the absence of perturbation : under stress there remains only one type of domain, parallel to the stress direction, and it shows LD.

In order to evaluate the LD under stress we have assumed that the effect of the exchange interaction on the excited state  ${}^3T_{1g}$  is small compared to the width of the vibronic bands and to the spin-orbit interaction. The excited levels  ${}^1T_{2g}$  and  ${}^1E_g$  are not split by exchange interaction.

At low temperature, the transitions essentially arise from the lowest states of the two sublattices,  $|{}^3A_2 - 1\rangle$  and  $|{}^3A_2 + 1\rangle$  which are equally populated. For a  $\sigma(\pi)$  transition in the first sublattice, there corresponds a  $\sigma(\pi)$  transition of equal intensity in the second sublattice and the two contributions to the LD under stress are equal (see table II for vibronic transitions). The LD under stress amplitude is given by  $\Delta A/A_m = (\Delta A_{m0}/A_m)f(\sigma)$  (see eq. (2.1)), since the transitions arise from the lowest state of the crystal. Then, following the above hypothesis, the LD under stress of  $\text{KNiF}_3$  would be very similar in shape to the MLD spectrum of  $\text{Ni}^{2+}/\text{KZnF}_3$  at low temperature.

**2.3 DISCUSSION.** — First we discuss the MLD spectrum of  $\text{Ni}^{2+}/\text{KZnF}_3$ . We have assigned the small peak located at  $14\,915\text{ cm}^{-1}$  to the zero-phonon  ${}^3A_{2g} \rightarrow {}^1E_g^a$  magnetic dipole transition. The corresponding  $f(\sigma)$  MLD signal is positive (Fig. 1) in agreement with our calculation (Table I). For other transitions, the oscillator strengths of the  ${}^3A_{2g} \rightarrow {}^1T_{2g}^a$  and  ${}^3T_{1g}(E)$  magnetic dipole lines are very weak [8] and we have not detected any corresponding MLD.

The temperature dependence of the MLD of the vibronic bands indicates that it is related to the  $\Delta A$  terms estimated in paragraph 2.2.3. The observed sign and amplitude of the MLD for  ${}^3A_{2g} \rightarrow {}^1E_g^a$  or  ${}^1T_{2g}^a$  (Fig. 1) agree with our calculations (Table III). Because of the positive sign of the MLD on the lowest energy side of the  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  transition (Fig. 1) we confirm that E is the lowest energy spin-orbit component of  ${}^3T_{1g}$  [5, 15]. The negative part of the MLD located around  $24\,500\text{ cm}^{-1}$  probably corresponds to that of the  $T_1$  and  $T_2$  spin-orbit components of  ${}^3T_{1g}$ .

If we eliminate the exciton-phonon magnon band of  $\text{KNiF}_3$  located at  $16\,158\text{ cm}^{-1}$ , which corresponds to no transition in the diluted compound, we can say that the shape of the LD under stress on  $\text{KNiF}_3$  below  $T_N$  (Fig. 2) is very similar to that of the MLD spectrum of  $\text{Ni}^{2+}/\text{KZnF}_3$  (Fig. 1). Thus we confirm the magnetic origin of the LD [1-3] and the spin orientation along the stress for  $\text{KNiF}_3$ . In the spectral region studied (Fig. 2) we have not detected any manifestation of the exchange interaction on the excited states, which is expected for spin forbidden transitions and which is consistent with our hypothesis for  ${}^3T_{1g}^b$ . Moreover, we made our experiments with an applied stress of  $250\text{ kgp.cm}^{-2}$  and we observed at low

temperature that  $\Delta A_m/A_m$  is close to  $\Delta A_{m0}/A_m$  (table III) for the LD of the  ${}^3A_{2g} \rightarrow {}^1E_g^a$  or  ${}^1T_{2g}^a$  vibronic transitions. This result, compared to formula (2.1), indicates that the crystal is untwinned under a stress of  $250\text{ kgp.cm}^{-2}$  [3].

**3. Cobalt compounds.** — **3.1 EXPERIMENTAL RESULTS.** — We have carried out the same type of experiments as for the nickel compounds on  $\text{Co}^{2+}/\text{KMgF}_3$  (1 %  $\text{Co}^{2+}$ ),  $\text{KCoF}_3$  and  $\text{RbCoF}_3$ . We have not detected any MLD ( $\Delta A_m < 5 \times 10^{-5}$ ) on a 2 mm thick crystal of  $\text{Co}^{2+}/\text{KMgF}_3$  at 1.6 K, under a 0.7 T magnetic field, in the spectral range  $13\,000$ – $23\,000\text{ cm}^{-1}$ . As for  $\text{KNiF}_3$  we have measured a relatively small LD under stress above  $T_N$  (Fig. 5) and a large LD below  $T_N$  (Fig. 6) on  $\text{KCoF}_3$ . In the

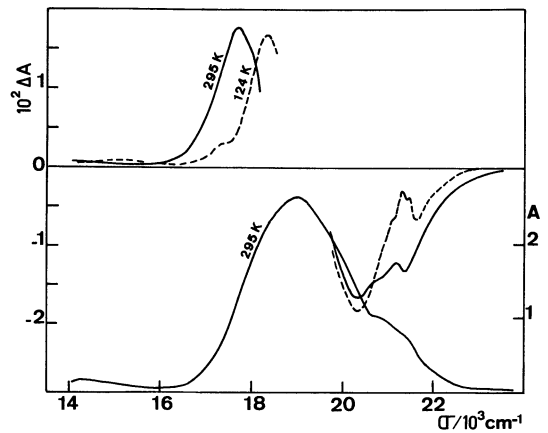


FIG. 5. — Absorption (bottom) and LD under stress ( $160\text{ kgp.cm}^{-2}$ ) spectra of  $\text{KCoF}_3$  above  $T_N$  (bandwidth  $\Delta\sigma = 15\text{ cm}^{-1}$ ). We do not represent the LD around  $19\,000\text{ cm}^{-1}$  because of the too large absorbance of the sample. The sample is  $0.46\text{ mm}$  thick.

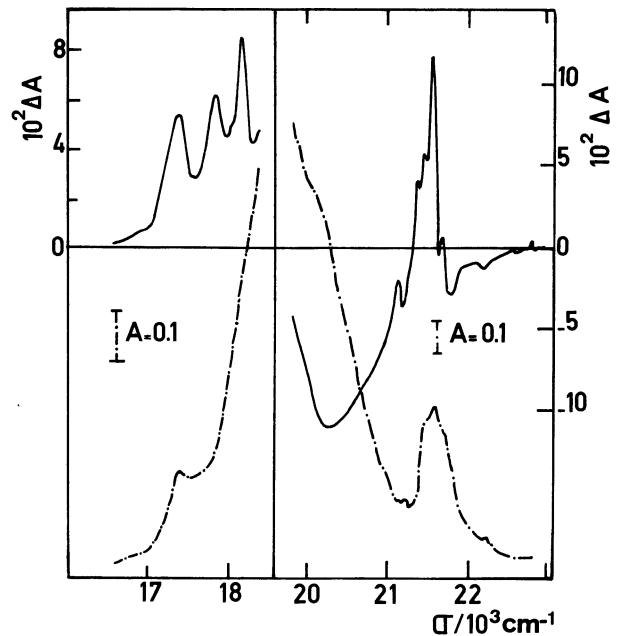


FIG. 6. — Absorption (—) and LD under stress ( $125\text{ kgp.cm}^{-2}$ ,  $S // \langle 001 \rangle$ ) spectra of  $\text{KCoF}_3$  at  $24\text{ K}$  (bandwidth  $\Delta\sigma = 10\text{ cm}^{-1}$ ). The sample is  $0.46\text{ mm}$  thick.

investigated spectral range the LD partly resolves the spin-orbit structure ( $E'$ ,  $E''$ ,  $U'_{3/2}$  and  $U'_{5/2}$  levels) of the excited states  ${}^4A_{2g}$ ,  ${}^2T_{1g}^a$ ,  ${}^2T_{2g}$ ,  ${}^4T_{1g}^b$ ,  ${}^2T_{1g}^b$  and  ${}^2A_{1g}$  in an  $O_h$  crystal field. The experimental values of the energy levels are compared to the theoretical results [16, 17] in table IV. The amplitude of the LD varies approximatively as the square of the sublattice magnetization with temperature. Similar results have been obtained on  $\text{RbCoF}_3$ .

TABLE IV

Theoretical and experimental energy levels for  $\text{KCoF}_3$

State	Calculated energy in $\text{cm}^{-1}$		Experimental energy in $\text{cm}^{-1}$ determined by LD
	from ref. [17]	from ref. [16]	
$E'$	0	0	
${}^4T_{1g}^a$ {			
$U'$	333		
$U'$	875		
$E''$	965		
${}^4T_{2g}$ {			
$E'$	7 417	7 178	
$U'$	7 459	7 221	
$U'$	7 556	7 316	
$E''$	7 745	7 506	
${}^2E_g$ {			
$U'$	10 965	10 930	
${}^4A_{2g}$ {			
$U'$	15 505	15 010	15 200
${}^2T_{1g}^a$ {			
$U'$	16 882	16 640	16 900
$E'$	17 394	17 165	17 400
${}^2T_{2g}$ {			
$U'$	17 560	17 292	17 800
$E''$	17 770	17 497	18 200
${}^4T_{1g}^b$ {			
$U'$	19 245	19 240	19 000-19 500
$E''$	19 247	19 240	
$U'$	19 327	19 297	
${}^2T_{1g}^b$ {			
$E'$	19 752	19 740	21 600
$U'$	21 730	21 544	
$E'$	21 864	21 619	
${}^2A_{1g}$ {			
$E'$	23 099	22 646	22 800

3.2 MLD CALCULATIONS. — For cobalt compounds, the absorbance is mainly due to vibronic transitions [16, 17] and for  $\text{KCoF}_3$  the exchange dipole transitions are very weak compared to single ion transitions between 13 000 and 23 000  $\text{cm}^{-1}$ .

First we consider the case of  $\text{Co}^{2+}/\text{KMgF}_3$ . The spin orbit coupling acting on the ground state level  ${}^4T_{1g}^a$  gives rise to four levels  $E'$ ,  $U'_{3/2}$ ,  $U'_{5/2}$ ,  $E''$ . The lowest level  $E'$  is fairly well isolated from  $U'$  located 333  $\text{cm}^{-1}$  above it (table IV). Then MLD *mixing terms* are small and we expect that there is no detectable MLD for broad bands as we shall verify experimentally. We recall in our case, that the *mixing terms* are due to the mixing of the wavefunction of the lowest state  $E'$  with  $U'_{3/2}$  and  $U'_{5/2}$  by the magnetic field, which can modify the transition probabilities for polarised light.

Let us discuss now the LD under stress of  $\text{KCoF}_3$  and  $\text{RbCoF}_3$ . If we assume that it is due to a *pure magnetic origin*, we shall demonstrate that the observed LD can only be explained by *mixing terms* due to the exchange interaction. In these compounds, the spin-orbit coupling is of the same order of magnitude as the exchange interaction.

It is therefore necessary to diagonalize the spin-orbit and the exchange interactions together [18] in order to deduce the eigenfunctions. At this step we note that for the magnetic  $\text{Co}^{2+}$  compounds we make our calculations in the molecular field approximation. In order to simplify our calculations, we have neglected the small tetragonal distortion which appears below  $T_N$ . The wavefunction of the lowest energy state in the first sublattice is thereby given by :

$$|\psi' \alpha'\rangle = a |T_1 - 1\rangle |U' \kappa\rangle + b |T_1 0\rangle |U' \lambda\rangle + c |T_1 1\rangle |U' \mu\rangle.$$

There is also the corresponding  $|\psi' \beta'\rangle$  level localised at the same energy in the second sublattice :

$$|\psi' \beta'\rangle = c |T_1 - 1\rangle |U' \lambda\rangle + b |T_1 0\rangle |U' \mu\rangle + a |T_1 1\rangle |U' \nu\rangle.$$

For the excited states, the value of the exchange field is unknown. However for the  ${}^4A_{2g}$  state, it is possible to know the wavefunctions of the sublevels split by exchange interaction.

TABLE V

Matrix elements for the  ${}^4T_{1g}^a \rightarrow {}^4A_{2g}$  magnetic dipole transition in the antiferromagnetic phase for  $\text{KCoF}_3$ . The  $a$ ,  $b$ ,  $c$  parameters are given in reference [18].  $E_0$  represents the difference in energy between the ground state and the barycentre of  ${}^4A_{2g}$ . The splitting  $\Delta$  is due to the exchange in the excited state  ${}^4A_{2g}(U)$ .  $\Delta A_m$  is evaluated for an antiferromagnetic exchange interaction in  ${}^4A_{2g}$ . For each mixing, the matrix elements have to be multiplied by the same reduced matrix element.

Energy	Matrix element	Mixing between ${}^4A_{2g}$ and ${}^4T_{1g}^a$		Mixing between ${}^4A_{2g}$ and ${}^4T_{2g}$	
		Matrix element value	$\Delta A_m$ for $\text{KCoF}_3$	Matrix element value	$\Delta A_m$ for $\text{KCoF}_3$
$E_0 + 3\Delta$	$\langle U' \mu   \hat{m}_-   \psi' \alpha' \rangle$	$-\frac{2}{\sqrt{15}}b + \frac{1}{\sqrt{30}}c$	+ 0.039	$-\frac{3}{\sqrt{10}}a - \frac{b}{\sqrt{5}}$	+ 0.033
$E_0 + \Delta$	$\langle U' \nu   \hat{m}_\beta   \psi' \alpha' \rangle$	0	0	0	0
$E_0 - \Delta$	$\langle U' \kappa   \hat{m}_+   \psi' \alpha' \rangle$	$\frac{3}{\sqrt{10}}a - \frac{1}{\sqrt{5}}b$	+ 0.231	$\frac{2}{\sqrt{15}}b + \frac{1}{\sqrt{30}}c$	+ 0.020
$E_0 - 3\Delta$	$\langle U' \lambda   \hat{m}_0   \psi' \alpha' \rangle$	$\frac{1}{\sqrt{5}}a + \frac{2}{\sqrt{15}}c$	- 0.244	$-\frac{c}{\sqrt{5}}$	- 0.009

We have examined more carefully the  ${}^4T_{1g}^a \rightarrow {}^4A_{2g}$  transition for which the LD can be completely calculated for the magnetic dipole transition and also for the phonon assisted band. We have still used the expressions (1) to (3) of appendix A.

Let us consider first the  ${}^4T_{1g}^a \rightarrow {}^4A_{2g}$  magnetic dipole transition which is allowed by the mixing of the  ${}^4A_{2g}$  state with  ${}^4T_{1g}^b$  (or  ${}^4T_{2g}$ ), or of the  ${}^4T_{1g}^a$  state with  ${}^4T_{2g}$ . We have calculated the LD, assuming that the spin orbit coupling mixes  ${}^4T_{1g}^b$  and  ${}^4T_{2g}$  predominantly to the excited state  ${}^4A_{2g}(U')$  (see table IV for energy separations). As an example, the magnetic dipole matrix elements are reported in table V for the first sublattice. For the second sublattice each component provides the same contribution to the LD, if we assume an antiferromagnetic exchange in  ${}^4A_{2g}$ . We therefore expect a negative and two positive LD signals for increasing energy (table V). If the exchange interaction in  ${}^4A_{2g}$  remains small, there should appear a  $f(\sigma)$  positive term in LD, coming from a mixing of  ${}^4A_{2g}$  with the  ${}^4T_{1g}^b$  or  ${}^4T_{2g}$  states. The signal would have the same amplitude and sign for a small ferromagnetic or antiferromagnetic exchange coupling in  ${}^4A_{2g}$ .

For exciton-phonon ( $\mathbf{k} = 0$ ) lines, by using the same type of calculations as those given for  $\text{KNiF}_3$ , we can deduce the expression of the LD corresponding to each transition from the ground level to the spin orbit components of the excited states. The case of the magnetic circular dichroism of  $\text{Co}^{2+}$  in the paramagnetic case has been treated by Harding and Briat [19]. In contrast to the  $\text{Ni}^{2+}$  ion, in the  $\Delta A/A_m$  MLD expression for most of the transitions, there remain several reduced matrix elements the value of which is not determined.

For the  ${}^4T_{1g}^a(\Psi') \rightarrow {}^4A_{2g}(U')$  transition the  $\Delta A/A_m$  ratio can be deduced theoretically without making any hypothesis upon the reduced matrix element values. The electric dipole matrix elements for the ( $\mathbf{k} = 0$ )  $t_{1u}$  phonon assisted transition towards each

$U'$  component split by exchange in the excited state are given in table VI.

If an antiferromagnetic exchange interaction is taken into account in  ${}^4A_{2g}$ , we expect to have a succession of one positive, one negative and one positive bands for an increasing photon energy in the LD under stress spectrum of the  ${}^4T_{1g}^a(\Psi') \rightarrow {}^4A_{2g}$  transition (see table VI).

If we assume that the exchange interaction in  ${}^4A_{2g}$  is null ( $\Delta = 0$ ) the LD arising from the two sublattices is identical and, at low temperature, the LD curve has the same shape as the absorption one, and :

$$\frac{\Delta A}{A_m} = \frac{\Delta A_{m0}}{A_m} f(\sigma) = \left[ \frac{a^2 + c^2 - 2b^2}{3(a^2 + c^2) + 2b^2} \right] \cdot f(\sigma) \quad (3.1)$$

Note that, in the absence of an exchange interaction in the ground state :  $a = 1/\sqrt{2}$ ,  $b = -1/\sqrt{3}$  and  $c = 1/\sqrt{6}$  and then  $\Delta A = 0$ . For  $\text{KCoF}_3$ , Buyers *et al.* [18] have deduced from neutron scattering experiments  $a = 0.856$ ,  $b = -0.470$ ,  $c = 0.215$  which leads to :

$$\Delta A_{m0}/A_m = +0.121.$$

The above results also apply to the vibronic broad band, as for  $\text{KNiF}_3$ .

In all cases the LD under stress would be large in  $\text{KCoF}_3$  and  $\text{RbCoF}_3$ , in contrast to the MLD in  $\text{Co}^{2+}/\text{KMgF}_3$  because of the exchange interaction in the ground state.

We indicate that the calculations are identical for  $\text{RbCoF}_3$  and  $\text{KCoF}_3$ . By using the coefficients  $a$ ,  $b$  and  $c$  calculated by Nouet [18b] we obtain  $\Delta A_{m0}/A_m = 0.109$  for  $\text{RbCoF}_3$ .

**3.3 DISCUSSION.** — For  $\text{KCoF}_3$  and  $\text{RbCoF}_3$  above  $T_N$ , the LD is related to the piezoelectric effect as in the case of the corresponding diluted compounds. Let us compare the LD under a  $\langle 001 \rangle$  stress in  $\text{KCoF}_3$  due to a  $D_{4h}$  lattice distortion (Fig. 5) to the

TABLE VI

Electric dipole matrix element values (in m units) and  $\Delta A_{m0}$  (in  $\text{m}^2$  units) for the  $\mathbf{k} = 0$   $t_{1u}$  phonons assisted  ${}^4T_{1g}^a(\Psi') \rightarrow {}^4A_{2g}(U')$  transition in the antiferromagnetic phase for  $\text{KCoF}_3$ . m is a reduced matrix element of the electric dipole moment. The parameters  $E_0$ ,  $\Delta$ ,  $a$ ,  $b$ ,  $c$ , are defined in table V. As in table V, the exchange is supposed to be antiferromagnetic in the excited state  ${}^4A_{2g}$ .

	First sublattice				Second sublattice				$\Delta A_{m0}$ for $\text{KCoF}_3$		
Energy	Matrix element	$\beta$	+	-	0	Matrix element	$\beta$	+		-	0
$E_0 + 3 \Delta$	$\langle \text{U}' \mu   \hat{m}_\beta   \psi' \alpha' \rangle$	0	$\frac{a}{\sqrt{6}}$	$\frac{a}{\sqrt{6}}$		$\langle \text{U}' \lambda   \hat{m}_\beta   \psi' \beta' \rangle$	$-\frac{a}{\sqrt{6}}$	0	$-\frac{a}{\sqrt{6}}$	$6.25 \times 10^{-2}$	
$E_0 + \Delta$	$\langle \text{U}' \nu   \hat{m}_\beta   \psi' \alpha' \rangle$	$\frac{b}{\sqrt{6}}$	$-\frac{b}{\sqrt{6}}$	0		$\langle \text{U}' \kappa   \hat{m}_\beta   \psi' \beta' \rangle$	$+\frac{b}{\sqrt{6}}$	$-\frac{b}{\sqrt{6}}$	0	$-3.68 \times 10^{-2}$	
$E_0 - \Delta$	$\langle \text{U}' \kappa   \hat{m}_\beta   \psi' \alpha' \rangle$	$\frac{c}{\sqrt{6}}$	0	$\frac{c}{\sqrt{6}}$		$\langle \text{U}' \nu   \hat{m}_\beta   \psi' \beta' \rangle$	0	$-\frac{c}{\sqrt{6}}$	$-\frac{c}{\sqrt{6}}$	$3.85 \times 10^{-3}$	
$E_0 - 3 \Delta$	$\langle \text{U}' \lambda   \hat{m}_\beta   \psi' \alpha' \rangle$	0	0	0		$\langle \text{U}' \mu   \hat{m}_\beta   \psi' \beta' \rangle$	0	0	0	0	



natural LD in  $\text{Rb}_2\text{Mg}(\text{Co})\text{F}_4$  [20] where the paramagnetic ion site symmetry is also  $D_{4h}$ . If we define by  $\pi$  the polarization of the light parallel to our stress direction, the sign of the LD of  $\text{KCoF}_3$  and  $\text{RbCoF}_3$  for each electronic excited level is the same as that obtained for  $\text{Rb}_2\text{Mg}(\text{Co})\text{F}_4$ . Therefore, we conclude that in  $\text{Rb}_2\text{Mg}(\text{Co})\text{F}_4$  there is a compression of the  $\text{F}^-$  octahedron around the  $\text{Co}^{2+}$  ions as for  $\text{KCoF}_3$  under stress. This fact disagrees with the result deduced by Ferguson *et al.* [20] from crystal field calculations.

Since the LD below  $T_N$  resolves the spin-orbit structure, it is interesting to compare the energy of the LD peaks (Fig. 6, 7) reported in table IV, to theoretical predictions including spin-orbit coupling. The agreement between them is not so bad if we consider that the theory does not include exchange interactions. Unfortunately as we can only calculate the LD for  ${}^4\text{A}_{2g}(\text{U})$  it is not possible to use the LD sign in order to make more reliable assignments of the spin-orbit components in the spectral range investigated.

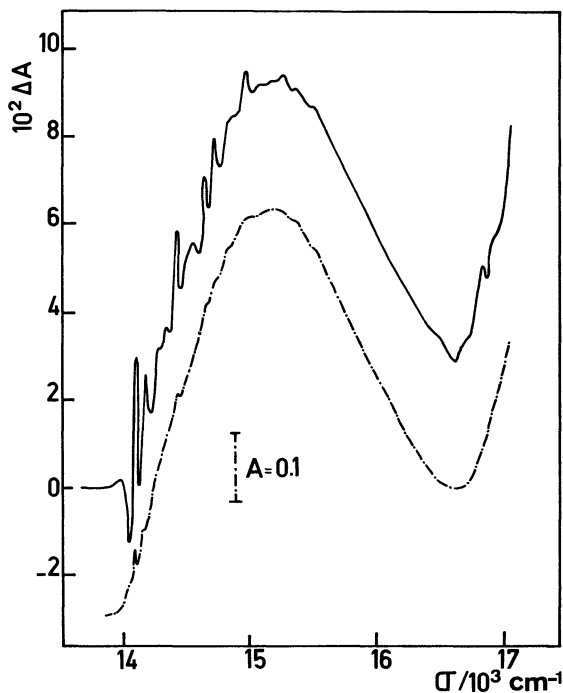


FIG. 7. — Absorption (—) and LD under stress ( $31 \text{ kgp.cm}^{-2}$ ,  $S // \langle 001 \rangle$ ) for the  ${}^4\text{T}_{1g}^a \rightarrow {}^4\text{A}_{2g}$  transition of  $\text{KCoF}_3$  at 8 K (bandwidth  $\Delta\sigma = 6 \text{ cm}^{-1}$ ). The sample thickness is 2.78 mm. The noise is less than  $10^{-4}$ .

Now we will discuss the LD for the  ${}^4\text{T}_{1g}^a \rightarrow {}^4\text{A}_{2g}$  transition (Fig. 7). First we look at the fine structure located at the low energy side of the band. If we suppose that there is no splitting in the excited state, the rather large negative signal at  $14\,050 \text{ cm}^{-1}$  cannot arise from the magnetic dipole transition, because the separation between this peak and the second positive one, which would be a vibronic sideband, is too weak (e.g.,  $40 \text{ cm}^{-1}$ ) compared to  $140 \text{ cm}^{-1}$ , the smallest frequency of the vibrational  $k = 0$  modes.

The separation of  $40 \text{ cm}^{-1}$  between the two lowest energy peaks observed in absorption and LD spectra is too large to come from the weak distortion in  $\text{KCoF}_3$ . Moreover, the orbital moment is quenched in the excited state. Consequently we may attribute this splitting to the exchange interaction in  ${}^4\text{A}_{2g}$  (tables V, VI). Thus the first LD peaks would correspond to the magnetic dipole transition or to the first one-phonon ( $t_{1u}$ ) electric dipole transition. The former assignment must be eliminated because of the smallness of the magnetic dipole strength of the  ${}^4\text{T}_{1g}^a(\psi') \rightarrow {}^4\text{A}_{2g}(\text{U})$  transition which has been calculated theoretically :

$$f_{\text{MD}} = 1.2 \times 10^{-12} [17] .$$

Note that, for the small shoulder located at  $14\,050 \text{ cm}^{-1}$  which would be one of the components of the transition, the experimental value of  $f$  is  $1.5 \times 10^{-11}$ . The absorbance value agrees with the electric dipole mechanism. Moreover the alternance of the signs (+ - +) for the three first LD peaks (Fig. 7) with frequencies  $14\,000$ ,  $14\,050$ ,  $14\,090 \text{ cm}^{-1}$  corresponds to an antiferromagnetic exchange  $\Delta \simeq 20 \text{ cm}^{-1}$  in the excited state (table VI).

If we assume an antiferromagnetic exchange interaction in  ${}^4\text{A}_{2g}$ , we should observe for the vibronic broad band a positive, a negative and a positive term for increasing energies. The nearly identical shape of the absorption and the LD curves for the vibronic sideband suggests that  $\Delta$  is weak compared to the width of the band. We evaluate a maximum value of  $20 \text{ cm}^{-1}$  for  $\Delta$ . A ferromagnetic exchange can also be considered ; it should not be larger.

In conclusion our results are consistent with an antiferromagnetic exchange of about  $20 \text{ cm}^{-1}$  in  ${}^4\text{A}_{2g}$ .

Since  $\Delta$  is weak compared to the vibronic band width, we can evaluate  $\Delta A_{m0}/A_m$  (expression of appendix B) by calculating the ratio of the experimental maximum values of  $\Delta A$  and  $A$  : 0.156.

This value is different from the theoretical one  $\Delta A_{m0}/A_m = +0.121$  previously determined in paragraph 3.2 by assuming that the spins align along the stress direction. A set of coefficients different from this of reference [18] should modify the calculated value of  $\Delta A_{m0}/A_m$ . For this reason, and since we have not taken into account the photoelastic contribution to the LD, we conclude that the agreement is reasonable between the theoretical and experimental values of  $\Delta A_{m0}/A_m$ .

In conclusion, the main contribution to the LD for the  ${}^4\text{T}_{1g}^a \rightarrow {}^4\text{A}_{2g}$  transition has a magnetic origin. The temperature dependence of the LD amplitude is found to be close to that of the square of the magnetization but we cannot explain well this behaviour because of the rather complicated expression of the  $a$ ,  $b$  and  $c$  coefficients versus the exchange field.

**4. Conclusion.** — Since a small uniaxial stress orients the spins in magnetically ordered crystals, we have been able to perform MLD measurements on  $\text{KNiF}_3$ ,  $\text{KCoF}_3$  and  $\text{RbCoF}_3$  in their antiferromagnetic phase, without an applied magnetic field. We therefore have interpreted for the first time the MLD of the exciton and exciton-phonon components for d-d transitions in 3d compounds.

In order to demonstrate the magnetic origin of the LD and to confirm spectroscopic attributions in the magnetic compounds, we have reported the MLD spectra of the diluted crystals  $\text{Ni}^{2+}/\text{KZnF}_3$  and  $\text{Co}^{2+}/\text{KMgF}_3$ . The observed MLD terms agree with our calculations in these paramagnetic compounds.

The LD spectrum under a  $\langle 001 \rangle$  stress obtained for  $\text{KNiF}_3$  can simply be compared to the MLD in  $\text{Ni}^{2+}/\text{KZnF}_3$ . In order to calculate the LD in antiferromagnetic  $\text{KNiF}_3$  where the lowest state is the only one populated, we may apply the MLD formula used for  $\text{Ni}^{2+}/\text{KZnF}_3$ . It is not the same case for cobalt compounds where  $\text{KCoF}_3$  shows LD under stress while  $\text{Co}^{2+}/\text{KMgF}_3$  gives no MLD because its ground state is a Kramers doublet. In  $\text{KCoF}_3$  the exchange field in the ground state which is of the same order of magnitude as the spin-orbit coupling, is at the origin of the observed LD.

Our results are consistent with a small exchange interaction in the excited states of the studied magnetic crystals. For example we have deduced an exchange splitting of some  $10 \text{ cm}^{-1}$  in the  $^4\text{A}_{2g}$  state of  $\text{KCoF}_3$ . For  $\text{Ni}^{2+}$  compounds our conclusion agrees with that of Ferguson *et al.* [15].

Moreover, since in the studied crystals, the multi-domain structure below  $T_N$  makes reproducible magneto-optical measurements such as MCD [22] difficult, this work illustrates how LD experiments under stress are efficient for spectroscopic assignments in cubic antiferromagnetic compounds.

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**Appendix A.** — We calculate the absorbance  $A$  in the absence of a magnetic field and the MLD  $\Delta A$  in terms of matrix elements of  $\hat{m}$  ( $\hat{m}$  stands for the magnetic or electric dipole moment) between the ground state  $I$  and the excited state  $J$ .

If we choose a system of axes  $X, Y, Z$ , parallel to the

fourfold axis of the crystal, the general expression of  $A$  for a cubic crystal is :

$$A = \frac{C}{\lambda_I} \sum_{I \rightarrow J} |\langle J | \hat{m}_Z | I \rangle|^2 \cdot f(\sigma) \quad (1)$$

$$A = A_m f(\sigma)$$

$\lambda_I$  stands for the degeneracy of the ground state  $I$ ,  $C$  is a constant depending upon the units.

In order to evaluate  $\Delta A$  under a magnetic field, we define a system of coordinates,  $0, +, -, [23]$  related to the direction of the magnetic field,  $\hat{m}_0$  being the component parallel to the magnetic field.

$$\Delta A = C \sum_{I \rightarrow J} N_I [|\langle J | \hat{m}_{\parallel} | I \rangle|^2 - |\langle J | \hat{m}_{\perp} | I \rangle|^2] \cdot f(\sigma) \quad (2)$$

For an electric dipole transition in a cubic crystal, it follows :

$$\begin{aligned} |\langle J | m_{\parallel} | I \rangle|^2 &= |\langle J | \hat{m}_0 | I \rangle|^2 \\ |\langle J | m_{\perp} | I \rangle|^2 &= \frac{1}{2} [|\langle J | m_+ | I \rangle|^2 + |\langle J | \hat{m}_- | I \rangle|^2] \end{aligned} \quad (3)$$

for a magnetic dipole transition we substitute  $\hat{m}_{\perp}$  to  $\hat{m}_{\parallel}$  and reciprocally in the two above equations.

**Appendix B.** — In order to obtain selection rules for vibronic transitions we must first reduce the space group representations for phonons at different points in the Brillouin zone into a sum of the  $\text{Ni}^{2+}$  site-group ( $O_h$ ) representations. If these representations are of odd parity, the corresponding phonons assist electric dipole transition between the ground state  $I_g$  and excited states  $J_g$ . The electric dipole moment for a transition between the  $i$ th vibronic level of  $I_g$  and  $j$ th level of  $J_g$  is given by :

$$\begin{aligned} \langle J_g j | \hat{m}_{\beta} | I_g i \rangle &= \sum_{S, \alpha} \times \\ &\times \left\{ \sum_{K_u} \left[ \frac{\langle J_g | \hat{m}_{\beta} | K_u \rangle \langle K_u | V_{S\alpha} | I_g \rangle}{W(I_g) - W(K_u)} \right. \right. \\ &\left. \left. + \frac{\langle J_g | V_{S\alpha} | K_u \rangle \langle K_u | \hat{m}_{\beta} | I \rangle}{W(J_g) - W(K_u)} \right] \langle i | Q_{S\alpha} | j \rangle \right\} \end{aligned} \quad (1)$$

where  $Q_{S\alpha}$  span through the component  $\alpha$  of the representations of the site symmetry group contained in the reduction of the space group representations of the phonons.  $V_{S\alpha}$  is the corresponding coefficient in the electron-lattice hamiltonian,  $\beta$  stands for the component of the electric dipole operator  $\hat{m}$  and  $W(X)$  is the energy of the  $X$  states.

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