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Piezospectroscopic studies of the triplet states of RbMnF_3

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Résumé. — Nous présentons ici une étude piézospectroscopique des bandes d'absorption de RbMnF_3 provenant des transitions optiques ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{I, II})$, ${}^4\text{T}_{2g}(\text{I, II})$. Nous en avons déduit les paramètres de couplage avec les modes de vibration E_g et T_{2g} pour la bande d'absorption ${}^4\text{T}_{2g}$ qui ne présente pas de structure fine. Nous avons analysé le comportement piézospectroscopique de la transition dipolaire magnétique ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{I})$ afin de déduire directement les paramètres de couplage associés dont la valeur est en bon accord avec nos calculs antérieurs.

Abstract. — We present piezospectroscopic studies of the absorption bands due to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{I, II})$, ${}^4\text{T}_{2g}(\text{I, II})$ optical transitions of RbMnF_3 . For the ${}^4\text{T}_{2g}$ unstructured absorption band we have deduced the coupling parameters involving the E_g and T_{2g} modes of vibration. The piezospectroscopic behaviour of the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{I})$ magnetic dipole transition is analysed to directly obtain the coupling parameters which are found to be in agreement with our previous calculations.

1. Introduction. — In previous papers [1-4], the experimental and theoretical study of Jahn-Teller effects in the four lowest orbital triplet excited states of Mn^{++} in RbMnF_3 was reported. These studies showed the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{I})$ transition at $\sim 22\,000\text{ cm}^{-1}$ to be unique in that it is always structureless as compared to other Mn^{++} transitions in antiferromagnetic materials which show a great deal of sharp structure below 20 K. This lack of structure which is difficult to interpret considering that the magnitude of the lattice interactions for the ${}^4\text{T}_{2g}(\text{I})$ state seems to be very similar to that of the highly structured ${}^4\text{T}_{1g}(\text{I})$ transition [3], precluded the detailed spectroscopic studies which were performed on the other transitions. However, from these detailed studies of the structured transitions, an approximate set of vibrational coupling parameters could be estimated for the ${}^4\text{T}_{2g}(\text{I})$ state. These were consistent with the predictions of the crystal field model and could account for the lack of sharp structure and generate the overall band shape of this transition.

The major part of this paper is concerned with the direct spectroscopic study of the ${}^4\text{T}_{2g}(\text{I})$ transition by means of a very sensitive method : the Stress induced Linear Dichroism (SLD), which often reveals the structure hidden under a broad band and is able to detect very weak absorption features. Further, even in the absence of induced structure, the SLD experiment can allow high resolution information on the vibrational coupling to be obtained from a moment analysis of the dichroism curves for stresses of appropriate symmetry. In the last part of this paper, we present SLD data on the other orbital triplet states with emphasis on directly determining the E_g and T_{2g} coupling parameters for the ${}^4\text{T}_{1g}(\text{I})$ transition from the weak magnetic dipole lines. This improves on the previous results [1-3] which had to be deduced from stress experiments on the spinwave sidebands.

2. Experimental. — RbMnF_3 has a cubic perovskite structure and orders antiferromagnetically along the three fold axes below $T_N \simeq 83\text{ K}$. The magnetostrictive strains ($\sim 10^{-6}$) can be neglected compared to the stress induced strains ($\sim 10^{-4}$) [5].

Several crystals were studied to eliminate artifacts coming from impurities present at low concentration. The analysis of the first crystal used is reported in

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reference [1] and a second crystal was lent to us by I. R. Jahn.

The experimental setup for SLD, described previously [6], allow us to detect extremely small differences in absorption ($\Delta k \simeq 10^{-4} \text{ cm}^{-1}$) in the considered spectral regions for 2 mm thick crystals. The SLD, $\Delta k = k_{\perp} - k_{\parallel}$, is defined as the difference of the extinction coefficients for light polarized perpendicular (σ) and parallel (π) to the applied stress. The samples were carefully polished with well defined parallel faces to a size of $4 \times 4 \times 2 \text{ mm}^3$. Indium sheets were used to distribute the stress uniformly over the sample.

3. Results and discussion. — **3.1 SLD OF THE ${}^4\text{T}_{2g}(\text{I})$ BAND.** — As emphasized previously, no sharp structure is revealed within the ${}^4\text{T}_{2g}(\text{I})$ absorption band (Fig. 1); however, two well chosen SLD

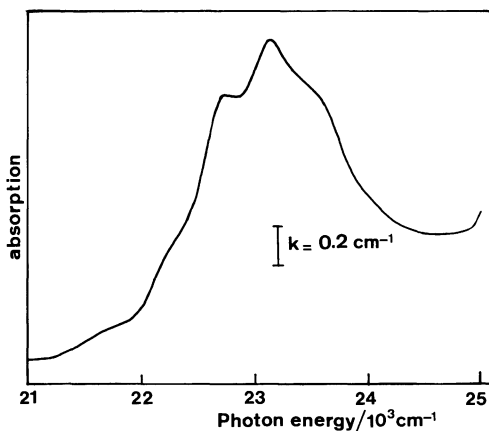


Fig. 1. — Absorption spectrum at 10 K of the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{I})$ transition. The sample thickness was 2.1 mm and the bandwidth $\Delta E = 15 \text{ cm}^{-1}$.

experiments, where the stress s is applied along a four-fold $\langle 001 \rangle$ and a three-fold $\langle 111 \rangle$ axis, are sufficient to determine the coupling parameters related to the E_g and T_{2g} modes of vibration. Consequently, we have performed the following set of experiments :

- $s \parallel \langle 001 \rangle$, $k \parallel \langle 100 \rangle$
- $s \parallel \langle 111 \rangle$, $k \parallel \langle 11\bar{2} \rangle$

where k stands for the unit vector along the direction of light propagation. Even if no sharp structure appears in the SLD spectra, it is always possible to extract these parameters from a moment analysis of the curves. The first order moments $\langle \Delta E \rangle_1$ of the SLD for $s \parallel \langle 001 \rangle$ and $s \parallel \langle 111 \rangle$ are, respectively, related to the coupling parameters involving E_g and T_{2g} modes [7]. In the following, we define the zeroth $\langle \Delta E \rangle_0$ and first order moments of the SLD (or the variation of zeroth and first order moments of the absorption under stress) as :

$$\begin{aligned} \langle \Delta E \rangle_0 &= 1/A \int (k_{\perp}(E) - k_{\parallel}(E)) dE/E \\ \langle \Delta E \rangle_1 &= 1/A \int (k_{\perp}(E) - k_{\parallel}(E)) (E - \bar{E}) dE/E \end{aligned} \quad (1)$$

where E is the photon energy, A the zeroth order moment of the absorption band defined by its area and \bar{E} its centre of gravity.

The $s \parallel \langle 001 \rangle$ spectra (Fig. 2) can be divided into two spectral regions. In the first regions ($21\,000$ – $21\,800 \text{ cm}^{-1}$ and $\sim 24\,600 \text{ cm}^{-1}$), a series of reasonably sharp lines are found (Fig. 2, a-d and l, m) for all samples studied. The amplitude of this structure is found to first increase with the applied stress up to $s_0 \simeq 400$ bars, then a slow decrease is observed up to

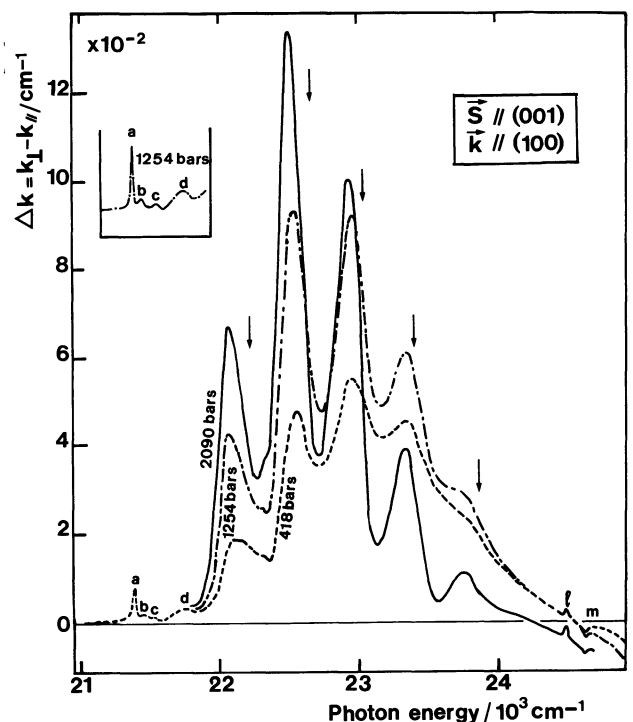


Fig. 2. — SLD spectra under a $\langle 001 \rangle$ stress at 10 K of the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{I})$ transition ($\Delta E = 15 \text{ cm}^{-1}$).

our highest stress values (2.09 kbars). s_0 corresponds exactly to the stress required to antiferromagnetically align all the spins along the stress direction [5]. However, the amplitude of the $s \parallel \langle 001 \rangle$ SLD spectra in these first regions is found to be quite sample dependent, and thus cannot be attributed to intrinsic RbMnF_3 absorption but must be due to impurities. It is well known that a very small amount of other 3d impurities in a Mn^{++} sample [8] produces absorption pair lines with noticeable intensity. Then, even with the high sensitivity associated with SLD, no magnetic dipole lines can be detected for the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{I})$ transition. We have reached the same conclusion from our magnetic circular dichroism

(MCD) studies of the ${}^4T_{2g}(I)$ band, another technique well suited to reveal weak magnetic dipole lines in antiferromagnets [9].

In the second spectral region (21 800-24 300 cm^{-1}) in contrast to the absorption spectrum in figure 1, a reasonably sharp progression in an $\sim 470 \text{ cm}^{-1}$ mode appears in the SLD spectra (Fig. 2). The SLD amplitude varies monotonically with the stress, and this part of the spectrum is quantitatively reproducible from sample to sample. The non-coincidence of the SLD extremes for $s \parallel \langle 001 \rangle$, with the maximum of the corresponding absorption components, visualized by arrows in figure 2, clearly indicates a large splitting of each component under stress. The stress induced splittings come from a sizeable coupling to E_g modes and will be analysed quantitatively below. In contrast, the SLD spectra for $s \parallel \langle 111 \rangle$ between 21 800 and 24 300 cm^{-1} (Fig. 3) is closer to the absorption dispersion curve (Fig. 1) and each SLD maximum corresponds exactly to one absorption component. This indicates qualitatively only a weak coupling of the transition to T_{2g} modes.

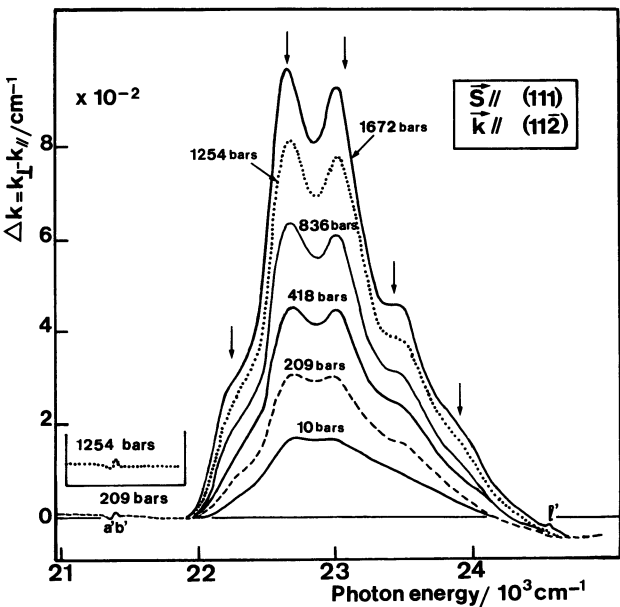


Fig. 3. — SLD spectra under a $\langle 111 \rangle$ stress at 10 K of the ${}^6A_{1g} \rightarrow {}^4T_{2g}(I)$ transition ($\Delta E = 15 \text{ cm}^{-1}$).

In the antiferromagnetic phase, the RbMnF₃ samples generally show a multidomain structure due to the equivalency between the four three-fold axes with respect to the spin configuration. In particular, it has been experimentally shown that in cubic perovskites [10], the twinned domain structure can be removed by a small stress (< 100 bars) applied along one of the spin directions. So in RbMnF₃, a small $\langle 111 \rangle$ stress induces a large modification of the spin structure before the microscopic spin flip arising in a single domain. On the other hand, a $\langle 001 \rangle$ stress is less effective in removing the domain

structure because of its symmetry with respect to the spin orientation. Consequently, below $s_0 \simeq 400$ bars, we expect that the SLD comes from the Voigt effect due to the spin reorientation and from the photoelastic effect. Above s_0 , the photoelastic part should be dominant.

The Voigt contribution cannot be neglected for all the RbMnF₃ absorption bands because the amplitude of the $s \parallel \langle 111 \rangle$ SLD spectra increases markedly below T_N when the temperature is lowered under a small stress (~ 20 bars) in spite of the very small magnetostriction [5]. Our measurements show that we obtain a single antiferromagnetic domain, the spin being parallel to the stress for $s \parallel \langle 111 \rangle \simeq 20$ bars. Such a behaviour was previously discussed for the cubic antiferromagnet KNiF₃ [10]. The non-vanishing SLD without applied stress, mainly seen for $s \parallel \langle 111 \rangle$ (Fig. 3) is due to the inequivalency between the four types of twinned domains arising from the internal strains. In this case, the baseline was determined above T_N and without stress. Consequently, we have only retained the data for stress values above $s_0 = 400$ bars where we have found a linear dependence of the photoelastic contribution with the stress.

No significant variation of the SLD has been found between 6 and 15 K, so the experimental results obtained here at 10 K, are similar to the low temperature data. The values of the zeroth $\langle \Delta E \rangle_0$ and first $\langle \Delta E \rangle_1$ moments of the SLD are reported in table I for $s \parallel \langle 001 \rangle$ and in table II for $s \parallel \langle 111 \rangle$.

Table I. — Values of the moments of the SLD under a $\langle 001 \rangle$ stress.

s/bars	$10^{-2} \langle \Delta E \rangle_0$	$\langle \Delta E \rangle_1/\text{cm}^{-1}$	$\langle \Delta E \rangle_1/\langle \Delta E \rangle_0/\text{cm}^{-1}$
418	4.0	— 4.1	— 102
836	6.25	— 5.8	— 93
1 254	5.8	— 12.5	— 215
1 672	5.5	— 18.4	— 335
2 090	5.2	— 25.1	— 483

Table II. — Values of the moments of the SLD under a $\langle 111 \rangle$ stress.

s/bars	$10^{-2} \langle \Delta E \rangle_0$	$\langle \Delta E \rangle_1/\text{cm}^{-1}$	$\langle \Delta E \rangle_1/\langle \Delta E \rangle_0/\text{cm}^{-1}$
10	1.1	— 1.8	— 163
209	2.0	— 3.7	— 185
418	3.06	— 5.0	— 164
836	4.1	— 8.0	— 195
1 254	5.25	— 9.75	— 186
1 672	6.3	— 11.7	— 186

In our case, the extraction of the coupling coefficients for E_g and T_{2g} modes is more complicated than for the F centre in alkali halides [7] because of the non-vanishing of $\langle \Delta E \rangle_0$. This seems to be mainly related to the Voigt effect for $s \parallel \langle 001 \rangle$ since $\langle \Delta E \rangle_0$ is nearly constant above 418 bars (Table I). The linear variation of $\langle \Delta E \rangle_0$ with the applied stress $s \parallel \langle 111 \rangle$ (Table II) may be due to the mixing of the wavefunc-

tions of the different Mn^{++} excited levels by the stress.

When $\langle \Delta E \rangle_0$ differs from zero, the first moment of the SLD, $\langle \Delta E \rangle_1$ defined by the expression (1) may be written as :

$$\langle \Delta E \rangle_1 = \langle \Delta E \rangle_0 \left[\frac{\int (k_{\perp}(E) - k_{\parallel}(E)) dE}{\int (k_{\perp}(E) - k_{\parallel}(E)) dE/E} - \bar{E} \right]. \quad (2)$$

The proportionality of $\langle \Delta E \rangle_0$ and $s \parallel \langle 111 \rangle$, even for a small value of s indicates that the Voigt effect is inefficient in that configuration. As can be seen qualitatively on the figure 3 the barycentre of the SLD curve is unaffected by the stress value so that the quantity between brackets of the expression (2) is taken to be a constant. This is quantitatively demonstrated by the nearly constant value of the ratio $\langle \Delta E \rangle_1 / \langle \Delta E \rangle_0$ reported in table II, whatever the value of the stress is. So, the variation with stress of the first moment of the SLD is only due to that of $\langle \Delta E \rangle_0$ and is not related, within our accuracy, to the splitting of the electronic levels by the stress. So following Schnatterly [7], we ascertain a weak coupling with T_{2g} modes in agreement with reference [3].

For $s \parallel \langle 001 \rangle$, because $\langle \Delta E \rangle_0$ has an origin other than that due to the direct effect of the applied stress, we are able to deduce, as did Schnatterly [7], the coupling coefficient V_{E_g} defined previously [3]. Following Schnatterly [7] and Solomon and McClure [3] :

$$V_{E_g} = -\frac{\sqrt{3}}{2} \times \frac{(c_{11} - c_{12})}{R} \times \frac{d(\langle \Delta E \rangle_1)}{ds}$$

where $c_{11} - c_{12} = 7.13 \times 10^{11}$ dynes/cm² [5] and $R = 2.125$ Å, the MnF bond length. From our experimental value for

$$d(\langle \Delta E \rangle_1)/ds = (14.6 \pm 1.5) \text{ cm}^{-1}/\text{kbar},$$

we have deduced $V_{E_g} = -(8.6 \pm 0.9) \times 10^{-5}$ dynes, a value quite close to the -7.2×10^{-5} dynes estimated earlier [3].

Thus, our results from direct spectroscopic studies on the ${}^4T_{2g}(\text{I})$ transition using SLD in combination with moment analysis are in quite good agreement with the estimates in reference [3], an E_g distortion of reasonable magnitude being necessary to understand the sensitivity of the ${}^4T_{2g}(\text{I})$ absorption to a $s \parallel \langle 001 \rangle$ stress. In strong contrast to the absorption band, the SLD spectrum exhibits a dominant progression in an $\sim 470 \text{ cm}^{-1}$ mode with a large Huang-Rhys factor. Because of this large Huang-Rhys factor the detection of pure excitonic lines is unlikely, particularly in a region of overlapping impurities (Fig. 2, a-d). This progression arises probably from the electric dipole exciton-magnon transition leading to the high intensity for this spin forbidden absorption

band and is constant with the results for the other transitions.

This 470 cm^{-1} mode was also found to dominate the absorption bands of the other orbital triplet states and has been assigned as the highest energy zone edge longitudinal optical (LO_3) lattice mode, which has predominantly A_{1g} cluster character at the Mn^{++} site [3]. Thus, the ${}^4T_{2g}(\text{I})$ state is also strongly coupled to A_{1g} modes leading to the large Huang-Rhys factor. This result is in agreement with references [3] and [4] where high order multiphonon processes are needed to explain the general ${}^4T_{2g}(\text{I})$ absorption bandshape.

Unfortunately, the absence of a detectable magnetic dipole line for the ${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{I})$ does not allow us to directly measure the coupling parameters contrary to the case of the other triplets as we shall see below.

3.2 SLD OF THE ${}^4T_{1g}(\text{I})$, ${}^4T_{2g}(\text{II})$ AND ${}^4T_{1g}(\text{II})$ BANDS. — Figures 4-7 report the results of SLD studies on the remaining orbital triplet states. In particular, our purpose was to compare the direct measurement of the shift of the e_1 and e_2 magnetic dipole origins of the ${}^4T_1(\text{I})$ state [1, 4] under an applied stress along $\langle 001 \rangle$ and $\langle 111 \rangle$ to that of the corresponding spin wave sidebands as reported earlier [1, 3]. The SLD allows this behaviour to be followed accurately to high stress (Figs. 4 and 5). Under 10 bars the weak residual SLD peaks (Fig. 4) indicate the e_1 and e_2 position to be $E_1 = 18\,220 \text{ cm}^{-1}$ and $E_2 = 18\,225 \text{ cm}^{-1}$ without stress. (One of the advantages of the SLD

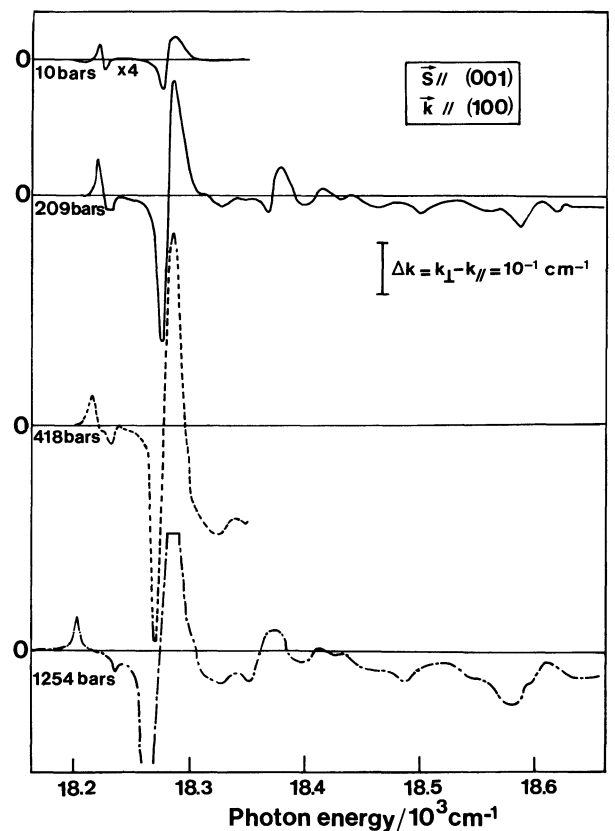


Fig. 4. — SLD spectra under a $\langle 001 \rangle$ stress at 10 K of the ${}^6A_{1g} \rightarrow {}^4T_{1g}(\text{I})$ transition ($\Delta E = 5 \text{ cm}^{-1}$).

experiments is that it gives an accurate estimate of the separation between two lines in contrast to polarized absorption measurements where two independent energy scans are necessary.) As found from direct absorption studies [2], the SLD is very large for the magnon sidebands located 60 cm^{-1} above the magnetic dipole origins. The e_1 and e_2 shifts differ significantly from those found experimentally from the sidebands (Table III), but are in closer agreement with the theoretical data [1] (Table III) and can be taken to refine the parameters such as V_{Eg} . This difference can be explained in terms of the interaction between the exciton and the magnon.

Table III. — Comparison between experimental and theoretical results for the shifts induced under a $\langle 001 \rangle$ stress.

Experiment	e_1 shift $\text{cm}^{-1}/\text{kbar}$	e_2 shift $\text{cm}^{-1}/\text{kbar}$	Average shift $\text{cm}^{-1}/\text{kbar}$
SLD	-13.9	+7.6	-3.3
Absorption magnon sideband	-18.4	+9.6	-9.1
Theory	-13.06	+8.57	-5.85

For $s \parallel \langle 111 \rangle$ (Fig. 5) and above s_0 , the SLD amplitude of the magnetic dipole lines decreases under stress. This can either be due to a broadening of the lines or to a decrease in their separation with increasing stress, the latter possibility being inconsistent with earlier measurements on magnetic dipole lines [1]. Our average shift, $-8 \text{ cm}^{-1}/\text{kbar}$, is in agreement with previous results [1].

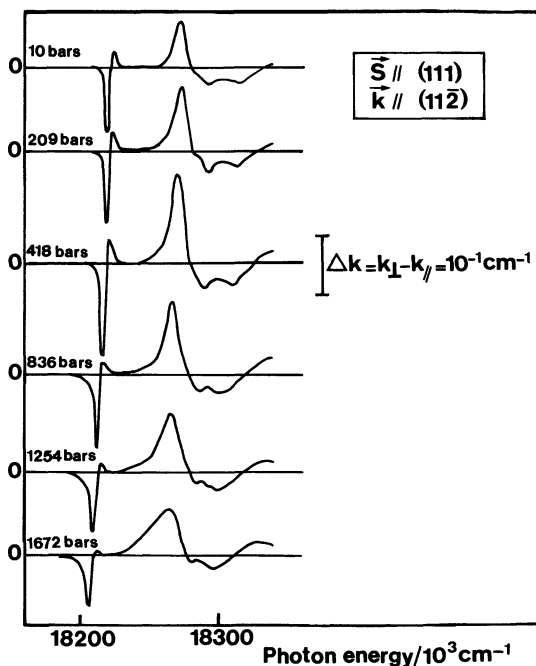


Fig. 5. — SLD spectra under a $\langle 111 \rangle$ stress at 10 K of the ${}^6A_{1g} \rightarrow {}^4T_{1g}(I)$ transition ($\Delta E = 5 \text{ cm}^{-1}$).

Our SLD measurements have not provided accurate measurements of the stress dependence of the magnetic dipole lines (Figs. 6, 7) located at $27\,877 \text{ cm}^{-1}$ for the ${}^6A_{1g} \rightarrow {}^4T_{2g}(II)$ transition [3] and at $32\,367$ and $32\,380 \text{ cm}^{-1}$ for the ${}^6A_{1g} \rightarrow {}^4T_{1g}(II)$ transition [3], mainly because of the weaker spectral resolution and of their broadening under large stress probably due to their sensitivity to the stress inhomogeneities.

The large and structured SLD around $27\,950 \text{ cm}^{-1}$ for the ${}^4T_{2g}(II)$ band (Fig. 6) and $32\,440 \text{ cm}^{-1}$ for the ${}^4T_{1g}(II)$ band (Fig. 7) reveals the complexity of the exciton-magnon bands which reflects both the splittings due to the spin-orbit coupling, the magnon density of states and the different symmetry of the involved exciton and magnon with respect to the photon energy.

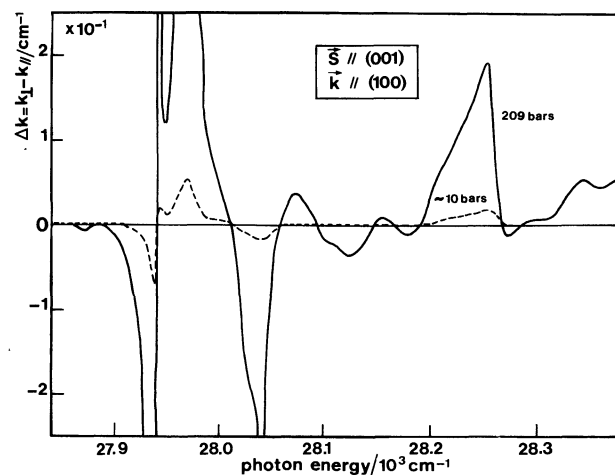


Fig. 6. — SLD spectra under a $\langle 001 \rangle$ stress at 10 K of the ${}^6A_{1g} \rightarrow {}^4T_{2g}(II)$ transition ($\Delta E = 7 \text{ cm}^{-1}$).

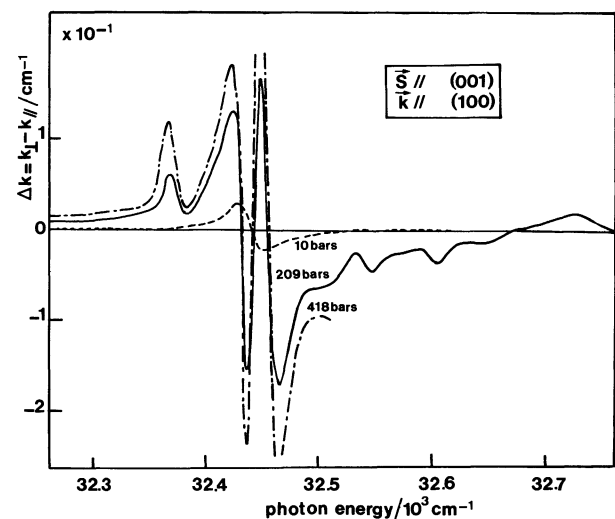


Fig. 7. — SLD spectra under a $\langle 001 \rangle$ stress at 10 K of the ${}^6A_{1g} \rightarrow {}^4T_{1g}(II)$ transition ($\Delta E = 10 \text{ cm}^{-1}$).

4. Conclusion. — We have studied the piezospectroscopic behaviour of the triplet states of RbMnF_3 giving rise to absorption bands in the visible and near

ultra-violet spectral range. The analysis of the SLD data of the non-structured absorption band due to the ${}^6A_{1g} \rightarrow {}^4T_{2g}(I)$ transition has shown unambiguously that this transition is weakly coupled to T_{2g} modes and strongly to E_g modes with

$$V_{E_g} = - (8.6 \pm 0.9) \times 10^{-5} \text{ dynes}.$$

This value is in agreement with that estimated previously from absorption measurements [3]. Unfortunately no intrinsic magnetic dipole line corresponding to the ${}^6A_{1g} \rightarrow {}^4T_{2g}(I)$ has been detected so as to provide a more direct determination of the Jahn-Teller effect.

Owing to the sensitivity of the SLD measurements we have measured the piezospectroscopic behaviour of the weak magnetic dipole lines due to the ${}^6A_{1g} \rightarrow {}^4T_{1g}(I)$ transition. Our data is in a better

agreement with the theory [2] than the results deduced on exciton-magnon bands [2] where the coupling between the exciton and the magnon and the exciton dispersion were neglected.

However no precise interpretation of the complicated structure appearing in SLD on exciton-magnon bands has been reported here and a detailed calculation of the SLD dispersion is needed. The lack of large SLD effects at energies higher than those of the exciton-magnon bands for all triplet states except $T_{2g}(I)$ is probably related to the less structured multiphonon band shape associated with a small mixing of the vibronic wavefunctions by the applied stress.

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