

ABSORPTION SPECTRUM OF MANGANOUS HALIDES TETRAHYDRATES IN THE ANTIFERROMAGNETIC STATES

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Résumé. — Nous avons observé le spectre d'absorption de $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ et de $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ entre 20 °K et 1,2 °K, afin d'étudier les états antiferromagnétiques par spectroscopie. Les champs moléculaires qui se déduisent des mesures du nombre d'onde en fonction de la température et de la polarisation en fonction du champ sont bien d'accord avec les résultats de Henry. La direction préférentielle des deux sels est l'axe c ou proche de l'axe c. Le champ seuil est entre 2 500 Ø et 5 000 Ø pour $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ et entre 7 500 Ø et 10 000 Ø pour $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, à 1,2 °K respectivement.

Abstract. — We have observed the absorption spectrum of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ between 20 °K and 1,2 °K in order to study the antiferromagnetic states spectroscopically. The molecular fields which are deduced from the measurements of wave number as a function of temperature and of spectral polarisation as a function of field are in good agreement with Henry's results. The preferred direction for the two salts is found to be the c-axis or near to the c-axis. The critical field is between 2,500 Ø and 5,000 Ø for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and between 7,500 Ø and 10,000 Ø for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ at 1,2 °K respectively.

When paramagnetic salts become antiferromagnetic, we can expect polarization and energy shift of the absorption spectrum. We have chosen the monoclinic crystals of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ as the Néel temperature T_N of these salts are easily obtained (1,6 °K and 2,2 °K respectively) [1], [2]. Furthermore the Mn^{2+} ions have line shape absorptions [3]. We measured the violet doublet absorption of these salts between 20 °K and 1,2 °K with a grating spectrograph with 2,5 Å per mm dispersion. We also observed the spin flopping phenomena with the magnetic field up to 23,000 Ø.

According to the theory of Tanabe and Sugano [4], the observed two line shape absorptions, the separations of which are 14 cm^{-1} in chloride and 9 cm^{-1} in bromide, are by the transition ${}^6\text{A}_1(d\epsilon^3 d\gamma^2) \rightarrow {}^4\text{A}_1$ or ${}^4\text{E}(d\epsilon^3 d\gamma^2)$ in cubic crystalline field which corresponds to the transition ${}^6\text{S} \rightarrow {}^4\text{G}$ in free ion. Even if the excited state is ${}^4\text{E}$, orbital degeneracy must be resolved

to give ${}^4\text{A}_1$, and ${}^4\text{A}_2$ due to the lower symmetry of the ligand C_{2v} in this case. It is probable that the excited state is the components of crystalline Stark splitting $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$ of ${}^4\text{A}_1$ or ${}^4\text{A}_2$.

The splitting of the ground state components $\pm \frac{5}{2}$, $\pm \frac{3}{2}$, $\pm \frac{1}{2}$ should be considered smaller than 0,1 cm^{-1} so that it is masked by line breadth $3 \sim 4 \text{ cm}^{-1}$.

According to X-ray analysis [5], space group of chloride is C_{2h}^2 and there are four molecules per unit cell. The ligand of manganous ion forms an octahedron of which two neighbour corners are occupied with Cl and others with H_2O . Its symmetry is near to C_{2v} and the 2-fold axis of one molecule is oriented almost along the b-axis. The overall axis of the four molecules, can be considered to be paralleled to the b-axis. We ascertained that there is no phase change at T_N by observation with parallel light and crossed Nicols.

TABLE I

RELATIVE INTENSITIES OF V_1 AND V_2

SALTS	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$						$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$					
	20 °K		4.2 °K		1.4 °K		20 °K		4.2 °K		1.6 °K	
Abs. Lines	V_1	V_2	V_1	V_2	V_1	V_2	V_1	V_2	V_1	V_2	V_1	V_2
$L \parallel b$, $E \parallel a$	4	5	4	6	4	2	40	40	40	40	25	25
$L \parallel b$, $E \parallel c'$	5	6	5	4	10	3	9	10	10	9	20	2
$L \parallel a$, $E \parallel b$	3	5	3	4	4	6	2	6	4	6	5	0
$L \parallel a$, $E \parallel c'$	5	6	5	4	10	3	8	9	8	6	20	2

1. Results in absence of field. — In Table 1, the relative intensities of V_1 and V_2 (designated from the longer wave length side) at different temperatures

are shown. There are considerable anisotropies in both salts, especially in bromide.

In the case of L (incident light) $\parallel a$, E (electric

vector of $L \parallel c'$ ($\perp a, b$) and in the case of $L \parallel b$, $E \parallel c'$, we obtain similar polarization so that these absorptions are caused by electric dipole. The measured oscillator strength is the order of 10^{-8} . Above and below T_N , we find remarkable changes of polarization. In the antiferromagnetic state, V_2 becomes very weak generally relative to V_1 . This should not occur if the excited state consists of two orbital components originating from 4E and it is probable that these are the crystalline Stark components $\pm \frac{3}{2}, \pm \frac{1}{2}$ of 4A_1 or 4A_2 .

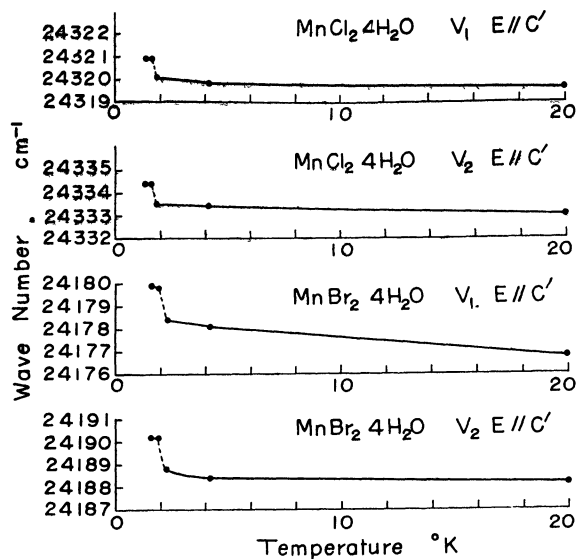


FIG. 1.

In fig. 1. temperature variations of the wave number of V_1 and V_2 are shown. Both lines shift to the shorter wave length by $0,9 \text{ cm}^{-1}$ in the chloride and by $1,5 \text{ cm}^{-1}$ in the bromide respectively from just above T_N .

Below T_N , both the ground and excited states should be in the molecular field which causes the splitting of spin components in each state. Firstly, we assume that the $\pm \frac{3}{2}$ component is lower in the excited states and the g -value is equal to 2. From Henry's magnetization data [2], the measured molecular field at $1,4 \text{ }^\circ\text{K}$ in the chloride is $9,000 \text{ }^\circ$ and at $1,6 \text{ }^\circ\text{K}$ in the bromide is $16,500 \text{ }^\circ$. These molecular fields cause splittings $0,84 \text{ cm}^{-1}$, $1,54 \text{ cm}^{-1}$ respectively between two neighbouring components $M_s, M_{s\pm 1}$.

Therefore the ratio of electron population is $10 : 4,4$ or $10 : 3,7$, respectively, for the two neighbouring components according to the Boltzmann distribution law. From these considerations, we can expect that the intensity maxima position of V_1 and V_2 shifts to shorter wave length by $0,84 \text{ cm}^{-1}$ or $1,54 \text{ cm}^{-1}$. The splitting must

be masked by the line width $3 \sim 4 \text{ cm}^{-1}$. Also it is probable that some distribution of the molecular field exists. The measured shifts are in good accordance with such expectation. For the polarization, if we suppose that the transition moments are not varied above and below T_N and take into consideration the electron population for each spin component, and the contamination of these spin components, the calculated intensity qualitatively explains the experimental results.

2. Results with field up to $23,000 \text{ }^\circ$. — Fig. 2 shows the polarization of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with magnetic field at $1,2 \text{ }^\circ\text{K}$. A, S and P designate the

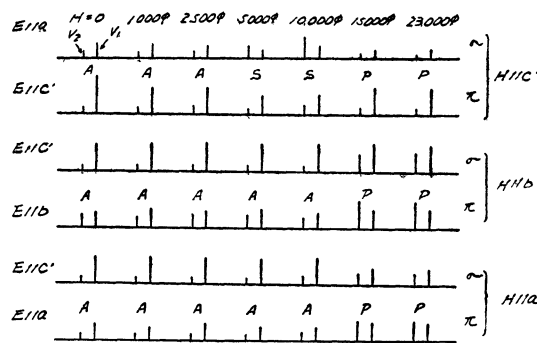


FIG. 2.

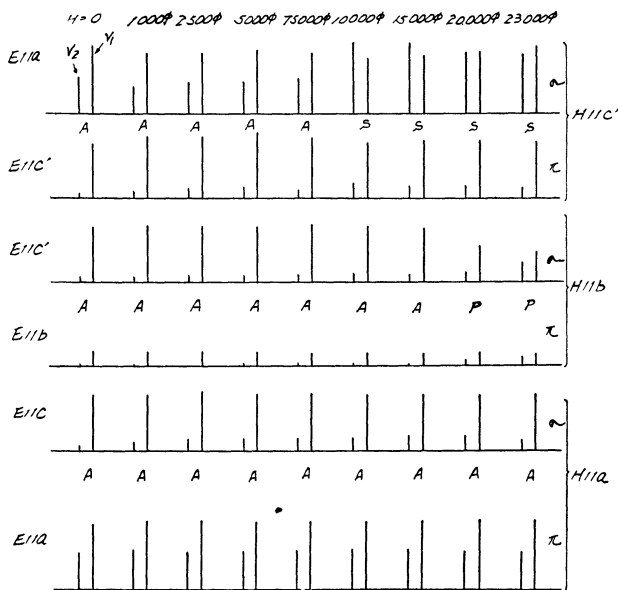


FIG. 3.

states considered to be antiferromagnetic, spin flopping and paramagnetic, respectively. When the magnetic field is parallel to the c' -axis and between $2,500 \text{ }^\circ$ and $5,000 \text{ }^\circ$, the spin flopping takes place. Furthermore between $10,000 \text{ }^\circ$ and

15,000 Oe , it returns to the P-state. The polarization of the S-state is similar to that of the P-state in the case of $\mathbf{H} \parallel a$, so that the spin direction seems to be close to the a-axis in the S-state. In the P-state, the spin is almost parallel to the magnetic field and it is reasonable that its polarization is similar to that of the A-state. When the magnetic field is parallel to the b- and a-axis and between 10,000 Oe and 15,000 Oe , it returns to the P-state. From the above results, it can be concluded that the c-axis or an axis near to the c-axis is the preferred axis. The molecular field of Henry's results at 1,2 $^{\circ}\text{K}$ is about 12,000 Oe and in agreement with our results.

Fig. 3 shows the polarization of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ with the magnetic field at 1,2 $^{\circ}\text{K}$. The general behavior is analogous to $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. When the magnetic field is parallel to the c'-axis and between 7,500 Oe and 10,000 Oe spin flopping takes place; Bölger [6] derives 8,800 Oe for the critical field at 1,4 $^{\circ}\text{K}$ from antiferroresonance experiments. Up to 23,000 Oe , it does not return to the P-state,

but when field increases, its polarization approaches to that of the A-state. When the magnetic field is parallel to the b-axis and between 17,000 Oe and 18,000 Oe , it returns to the P-state. When the field is parallel to the a-axis, it does not return to the P-state in our maximum field. The molecular field of Henry's results is about 17,500 Oe at 1,2 $^{\circ}\text{K}$ and in agreement with our results in the case of $\mathbf{H} \parallel b$. The anisotropy is more pronounced than $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. The preferred axis is the c-axis or near to the c-axis in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

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