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ABSORPTION SPECTRUM OF MANGANOUS HALIDES TETRAHYDRATES IN THE ANTIFERROMAGNETIC STATES

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Résumé. — Nous avons observé le spectre d’absorption de MnCl₂·4H₂O et de MnBr₂·4H₂O 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 MnCl₂·4H₂O et entre 7 500 Ø et 10 000 Ø pour MnBr₂·4H₂O, à 1,2 °K respectivement.

Abstract. — We have observed the absorption spectrum of MnCl₂·4H₂O and MnBr₂·4H₂O 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 MnCl₂·4H₂O and between 7,500 Ø and 10,000 Ø for MnBr₂·4H₂O 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 MnCl₂·4H₂O and MnBr₂·4H₂O as the Néel temperature $T_N$ of these salts are easily obtained (1,6 °K and 2,2 °K respectively) [1], [2]. Furthermore the Mn²⁺ 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 spectrographe 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 $^6A_1(d^5_e \gamma d\gamma) \rightarrow ^4A_1$ or $^4E(d^5_e \gamma d\gamma)$ in cubic crystalline field which corresponds to the transition $^6S \rightarrow ^6G$ in free ion. Even if the excited state is $^4E$, orbital degeneracy must be resolved to give $^4A_1$ and $^4A_2$ due to the lower symmetry of the ligand $C_2$ 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 $^4A_1$ or $^4A_2$.

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 $3 \sim 4$ cm⁻¹.

According to X-ray analysis [5], space group of chloride is $C_{2h}$ 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>
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<td>Relative intensities of $V_1$ and $V_2$</td>
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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) I/ a, E (electric
vector of $L \parallel e'(c' \perp a, b)$ 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 $10^{-6}$. 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 $^4A_2$.

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 $^4A_2$.

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 cm$^{-1}$ in the chloride and by 1,5 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 °K in the chloride is 9,000 ° and at 1,6 °K in the bromide is 16,500 °. These molecular fields cause splittings 0,84 cm$^{-1}$, 1,54 cm$^{-1}$ respectively, between two neighbouring components $M_\pm, M_{\pm \pm}$.

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 cm$^{-1}$ or 1,54 cm$^{-1}$. The splitting must be masked by the line width 3 ~ 4 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 °. — Fig. 2 shows the polarization of MnCl$_2$.4H$_2$O with magnetic field at 1,2 °K. $A$, $S$ and $P$ designate the
15,000 $\Theta$, 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 $\Theta$ and 15,000 $\Theta$, 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 oK is about 12,000 $\Theta$ and in agreement with our results.

Fig. 3 shows the polarization of MnBr$_2$.4H$_2$O with the magnetic field at 1,2 oK. The general behavior is analogous to MnCl$_2$.4H$_2$O. When the magnetic field is parallel to the c'-axis and between 7,500 $\Theta$ and 10,000 $\Theta$, spin flopping takes place; Bölinger [6] derives 8,800 $\Theta$ for the critical field at 1,4 oK from antiferroresonance experiments. Up to 23,000 $\Theta$, 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 $\Theta$ and 18,000 $\Theta$, 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 $\Theta$ at 1,2 oK and in agreement with our results in the case of $\mathbf{H} \parallel b$. The anisotropy is more pronounced than MnCl$_2$.4H$_2$O. The preferred axis is the c-axis or near to the c-axis in MnCl$_2$.4H$_2$O.

REFERENCES

[1] Friedberg (S. A.) and Wasscher (J. D.), Physica, 1953, 19, 1072.