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INFLUENCE OF THE ANTIFERROMAGNETIC ORDERING ON THE OPTICAL ABSORPTION SPECTRUM OF MANGANESE CARBONATE CRYSTALS

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The optical absorption spectrum of $MnCO_3$ crystals was investigated in the temperature range between 4 and 300°K. Narrow bands were observed, due to the transitions $^6S_{5/2} \rightarrow {}^4G_{3/2}$, $^4D_{3/2}$ and $^4P_{3/2}$ in the Mn^{2+} ion. It is shown that the temperature shift of the frequencies of all the optical absorption bands increases greatly on approaching the Néel point. It was found that the $^6S_{5/2} \rightarrow {}^4D_{3/2}$ band narrowed on cooling below the Néel temperature (29.4°K).

THE influence of the antiferromagnetic ordering on the structure of the optical absorption spectrum was investigated in the greatest detail for manganese fluoride crystals.[1-3] It was shown that the rate of the temperature shift of the absorption bands on the frequency scale was trebled below the Néel point [1,2] and that the widths of the bands decreased sharply. The former effect was ascribed [1] to the increasing role of the exchange interaction, which displaced to a different extent the ground, ^6S, and the excited, ^4G, ^4D, etc., energy levels of the Mn^{2+} ion. The latter effect was connected [3] to the predominance, in the antiferromagnetic state, of the interaction with spin waves over the electron-phonon interaction.

Crystals of manganese fluoride MnF_2 have a tetragonal lattice D_{4h}^{14} and a simple magnetic structure with the ordering directed along the fourfold axis. To check the generality of the influence of the antiferromagnetic ordering discovered for MnF_2, it was of interest to carry out similar investigations on the absorption spectra of manganese compounds having other crystal and antiferromagnetic structures. We describe below the results of an investigation of the optical absorption spectra of $MnCO_3$ crystals having the D_{3d}^6 crystal lattice, which is retained below the Néel point $T_N = 29.4$°K, with the ordered spins lying in a plane perpendicular to the threefold axis.

Before presenting and discussing the results, we shall remark on the methodology. The absorption spectra were photographed with a diffraction spectrograph DFS-8 having a linear dispersion of 6 Å/mm, and the absorption intensity was measured by photographic photometry.[4] The samples were cooled in a metal cryostat with transparent quartz windows [5]—the construction of this cryostat allowing us to cool the sample either with liquid helium (hydrogen) or with its vapor. In the latter case, it was possible to vary the temperature of the test sample by varying the intensity of the incident light. The exposure was varied to ensure the recording of a sharp spectrogram. Above 20°K, the temperature was checked with a copper-constantan thermocouple. The measurements were carried out in polarized light but since all the samples had a growth surface perpendicular to the threefold axis, the variation of the direction of the polarization had no marked effect.

The optical absorption spectrum of $MnCO_3$ crystals is very similar to the spectrum of MnF_2 crystals.[1-3,6] The table below lists the frequencies of the observed absorption bands both for MnF_2 and $MnCO_3$ at $T = 20.4$°K. It is easily seen that all the observed MnF_2 bands are shifted by approximately the same amount toward the ultraviolet with respect to the corresponding $MnCO_3$ bands.

This similarity of the spectra is another proof that the observed bands are due to the optical transitions between the energy levels of the unfilled d-shell of the Mn^{2+} ion.

Starting from this conclusion and from the results of a comparison with calculations of the Mn^{2+} ion spectrum (both free and in a field of cubic symmetry [7-9]), we identified the optical transitions (the results are also given in the table).

Table I. Absorption spectra of MnF_2 and $MnCO_3$ crystals at T = 20.4°K (Δ is the difference between the frequencies of the corresponding bands of MnF_2 and $MnCO_3$ crystals; ν and Δ are given in cm^{-1})

Transition	MnF_2	$MnCO_3$	Δ
$^6S_{5/2} \to {}^4G_{3/2}$	$\nu = 25304$	$\nu = 24575$	729
	$\nu = 25449$	$\nu = 24620$	729
$^6S_{5/2} \to {}^4D_{3/2}$ (1)	$\nu = 28028$	$\nu = 27249$	779
		$\nu = 27278$	750
$^6S_{5/2} \to {}^4D_{3/4}$ (2)	$\nu = 30425$		
	$\nu = 29930$	$\nu = 29199$	731

We shall not consider here the special features of the absorption spectrum of $MnCO_3$. A detailed analysis of the spectrum taking into account the influence of the spin-orbit interaction and the noncubicity of the crystal field will be given elsewhere. Here, we note only that although all the considered optical transitions are forbidden from the point of view of spin ($\Delta S \neq 0$), they are observed to have very different intensities but always much greater than the intensity of the corresponding transitions in MnF_2 crystals. This means that even when very thin samples are used ($d \leq 0.4$ mm) we can analyze the structure of the most intense transitions $^6S_{5/2} \to {}^4G_{3/2}$, $^6S_{5/2} \to {}^4D_{3/2}$ (2) only at helium temperatures. The structure of the weakest transition $^6S_{5/2} \to {}^4D_{3/2}$ (1) could be analyzed over a wide range of temperatures.

At sufficiently low temperatures near the Néel point ($T_N = 29.4$°K) and below this point, a close doublet is observed in the region of the latter transition (cf. the table), the long-wavelength component of which is several times more intense than the short-wavelength component (Fig. 1). This particular band was investigated in the greatest detail. As for some of the absorption bands of MnF_2, we found that the $^6S_{5/2} \to {}^4D_{3/2}$ (1) transition band narrowed strongly on cooling $MnCO_3$ below the Néel point (Fig. 2), indicating that the observed effect of antiferromagnetic ordering is a general one. At the same time, it should be noted that close to T_N no anomaly was observed in the temperature dependence of the bandwidths of the transitions $^6S_{5/2} \to {}^4G_{3/2}$ and $^6S_{5/2} \to {}^4D_{3/2}$ (2). This may be due to a complex structure, which we were unable to resolve.

The lack of resolution of the structure of the investigated optical transitions should not greatly distort the temperature dependence of the frequency shift of the bands provided all the components of the structure are shifted in the same way on cooling. In fact, for all the optical transitions in $MnCO_3$, we observed a sharp rise of the rate of the temperature shift of the frequencies of the absorption band maxima on approaching to the Néel point. Figure 3 shows that this effect is approximately the same for all the transitions. Attention is drawn to the fact that the beginning of this increase of the frequency shift lies much higher than T_N. The magnitude of the frequency shift of the bands in the region of T_N can be estimated by assuming that it is related to the Zeeman splitting in an effective exchange field H_E. Such an estimate [11] gives a value close to the experimental value of the shift $\Delta\nu$.

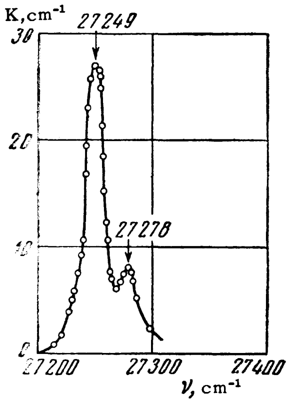

FIG. 1

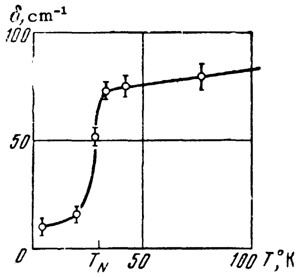

FIG. 2

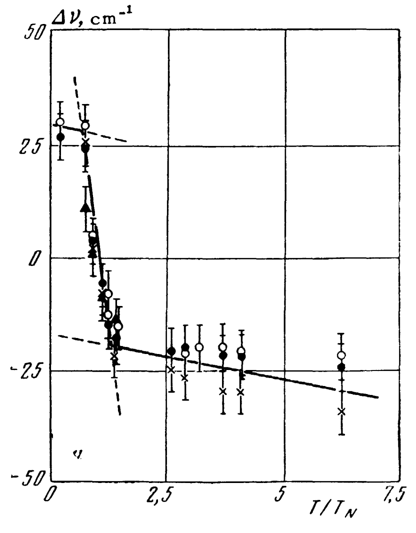

FIG. 1. Doublet of the transition $^6S_{5/2} \to {}^4D_{3/2}$ (1) at T = 20°K.

FIG. 2. Temperature dependence of the band half-width of the transition $^6S_{5/2} \to {}^4D_{3/2}$ (1) near the Néel point T_N.

FIG. 3. Temperature dependence of the frequency shift of the optical absorption maxima for various transitions in $MnCO_3$: ×, ● – $^6S_{5/2} \to {}^4G_{3/2}$ doublet; ▲ – $^6S_{5/2} \to {}^4D_{3/2}$ (1); ○ – $^6S_{5/2} \to {}^4D_{3/2}$ (2); $T_N = 29.4$°K.[10]

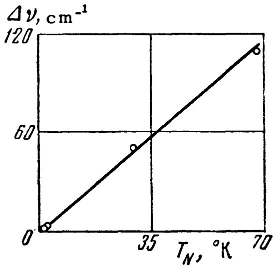

FIG. 4. Dependence of the frequency shift of the ${}^6S_{5/2} \to {}^4G_{3/2}$ band in the antiferromagnetic region on the ordering temperature of various crystals: MnF_2 [6] ($T_N = 68$°K); $MnCO_3$ ($T_N = 29.4$°K), present work; $MnBr_2 \cdot 4H_2O$ [12] ($T_N = 2.16$°K); $MnCl_2 \cdot 4H_2O$ [12] ($T_N = 1.6$°K).

A similar anomalous frequency shift of the band maxima as a result of the antiferromagnetic ordering of MnF_2 was observed by Finlayson et al.,[2] and by the present authors;[6] the effect was also reported for $MnCl_2 \cdot 4H_2O$ and $MnBr_2 \cdot 4H_2O$ by Tsujikawa.[12] It was found that the magnitude of the anomalous shift in the antiferromagnetic region was directly proportional to T_N (Fig. 4). The regularity of the relationship between $\Delta\nu$ and T_N for various crystals confirms once again the important influence of the exchange interaction on the optical spectra of antiferromagnets.

In conclusion, we take this opportunity to thank Professor B. I. Verkin and Professor A. S. Borovik-Romanov for their interest in this work and for their support.

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