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OPTICAL ABSORPTION SPECTRA OF Mn^{2+}, Co^{2+}, Ni^{2+}, *AND* Ho^{3+} *IN ANTIFERROMAGNETIC CRYSTALS*

A. I. BELYAEVA, V. V. EREMENKO, N. N. MIKHAĬLOV, and S. V. PETROV

Institute for Physics Problems, Academy of Sciences, U.S.S.R.; Physico-technical Institute of Low Temperatures, Academy of Sciences, Ukrainian S.S.R.

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Some features of the growth of MnF_2 single crystals alloyed with Co, Ni, and Ho ions are reported. An analysis of the optical absorption spectra indicates that the added ions enter the MnF_2 lattice. It is also shown that the antiferromagnetic transition of the solvent crystal is accompanied by an anomalous shift of the optical absorption bands of added Mn^{2+} and Co^{2+} ions towards the shorter waves, together with pronounced narrowing that is of the same order as for the bands of pure MnF_2 or CoF_2 crystals. The absorption lines of Ho ions are not affected by the antiferromagnetic transition of MnF_2.

MAGNETIC ordering causes certain characteristics of the optical absorption spectra of antiferromagnetic crystals[1-9] such as the fluorides of Mn,[1,2,6,8] Co,[9] and Ni.[5] There has previously been no basis for affirming that excitation in these crystals will be localized in light-absorbing ions without resonant transfer to the nearest unexcited ions of the same metal, thus forming Frenkel excitons.[10] However, to understand the characteristics of magnetically-ordered crystal spectra it is evidently important to know whether these are only exciton spectra or will include localized impurity absorption bands. It is therefore important to investigate the spectra of antiferromagnetic crystals alloyed with transition or rare-earth metals. The latter are especially interesting, because the absorption bands of rare earth ions in crystals are usually narrow, thus permitting investigations within a broad temperature range.

We here report the first, to our knowledge, attempt to alloy MnF_2 single crystals with holmium, and also to grow fluorides containing two different transition metal ions, Mn^{2+} and Co^{2+} or Mn^{2+} and Ni^{2+}. The absorption spectra of these crystals are investigated from 4.2° to 100°K, and their characteristics near the magnetic ordering temperature of the solvent crystal are discussed.

1. GROWING OF MIXED CRYSTALS

Single crystals of pure transition-metal fluorides were obtained using the procedure described in[11]. The growing of mixed single crystals encounters several additional difficulties. Melting diagrams of the MnF_2—CoF_2 and MnF_2—NiF_2 binary systems are not available; therefore the respective working temperatures had to be selected experimentally. It could be assumed that MnF_2, CoF_2, and NiF_2 are mutually soluble in any ratio, because their tetragonal lattice parameters and ion radii are very similar (Table I). When MnF_2 + Ho single crystals are grown, additional difficulties arise because HoF_2 does not exist independently (the valence of Ho is 3+); we therefore had to consider HoF_3, which has a hexagonal lattice that differs considerably from the tetragonal lattice of MnF_2 (Table I).

We obtained the following mixed single crystals:

$$MnF_2 + 10\%\ CoF_2,\ CoF_2 + 10\%\ MnF_2,\quad MnF_2 + 10\%\ NiF_2,\ MnF_2 + 1\%\ Ho. \qquad (1)$$

The raw materials for the mixed single crystals $MnF_2(x)CoF_2(1-x)$ were powdered pure MnF_2 and CoF_2 single crystals which were mixed thoroughly in an agate mortar. To obtain single crystals of MnF_2 + 10% NiF_2 we used a mixture of finely crystalline MnF_2 and NiF_2 baked in a hydrogen fluoride atmosphere. To obtain single crystals of MnF_2 + 1% Ho, fluoric acid was added to a mixture of Ho_2O_3 and $MnCO_3$. The subsequent treatment of the fluoride mixtures was the same as the treatment of pure powdered MnF_2,[11] in order to obtain the raw material for growing single crystals.

When MnF_2 is alloyed with Co, Ni, or Ho ions there is no danger that the alloyed fluorides will evaporate near the melting point (~ 930°C) of MnF_2;

Table I. Physical and Chemical Properties of Mn, Co, Ni, and Ho Fluorides

Crystal	Molecular weight	Density, g/cm³	Melting point, °C	Lattice	Lattice parameters, Å a	b	c	Ion radius, Å[17]
MnF_2	92.94	3.92 [12] 3.98 [17]	929.5±0.5 [12] 930 [13] 856 [17]	Tetragonal[17]	4.87 [16]	—	3.31 [16]	0.91 0.8
CoF_2	96.94	—	1200 [13]	Tetragonal[17]	4.69 [16]	—	3.19 [16]	0.82 0.72
NiF_2	96.71	4.63 [17]	1450 [13] 1420 [14]	Tetragonal[17]	4.71 [16]	—	3.11 [16]	0.78 0.69 0.74
HoF_3	221.92	7.644 [15] 7.829 [15]	1380 [15]	Orthorhombic[15] Hexagonal[15]	6.404 [15] 6.833 [15]	6.875 [15] —	4.379 [15] 6.984 [15]	0.86

therefore the composition of the original mixture was determined by weight.

When mixed single crystals were grown the melt was maintained somewhat longer than in the case of pure MnF_2 at a high temperature, before reaching the working regime of the furnace.[11] This was required for the better dissolution of the solid phase of added fluorides in the MnF_2 melt; Table I shows that the melting point of MnF_2 is lower than that of CoF_2, NiF_2, or HoF_3. The temperature of the MnF_2 + 10% CoF_2 melt was ~1000°C; the corresponding working temperature of the furnace was ~1050°C.

When growing MnF_2 + 10% NiF_2 single crystals the temperature in the hottest furnace zone was maintained at 1150°C. Since the viscosity of molten CoF_2 is less than that of MnF_2 (while the volatility of the former is considerably greater) and it does not capture HF bubbles while solidifying, the CoF_2 + 10% MnF_2 melt was not prepared in a vacuum. In the latter case the temperature of the hottest furnace zone was maintained at about 1220°C. The final transparent single crystals were cones ~30 mm high with ~10-mm base diameters. The single crystals of MnF_2 were pale pink and those of CoF_2 were dark red; the mixed $MnF_2(x)CoF_2(1 - x)$ single crystals were also transparent, with coloration depending on their composition; the MnF_2 + 10% NiF_2 single crystals were yellow-orange.

Holmium dissolves very poorly in MnF_2. We obtained two types of MnF_2 + 1% Ho single crystals. The first type was grown in a hydrogen fluoride atmosphere. In the lower part of the crucible the crystal was transparent, pale pink, pure MnF_2; the entire Ho admixture appeared as a white blob, only very slightly dissolved, that had been squeezed into the upper part of the crucible. This obviously resulted from the fact that there had been no local compensation of excess charge resulting from the substitution of trivalent Ho for Mn^{2+}. Crystals of the second type were grown under hydrogen fluoride with a slight oxygen inflow; the dissolution was then considerably improved. The excess charge was obviously compensated by isomorphic substitution of O^{2-} for the F^- ions that were nearest the Ho^{3+} ions. This substitution was facilitated by the very similar radii of F^- and O^{2-}, which are 1.33

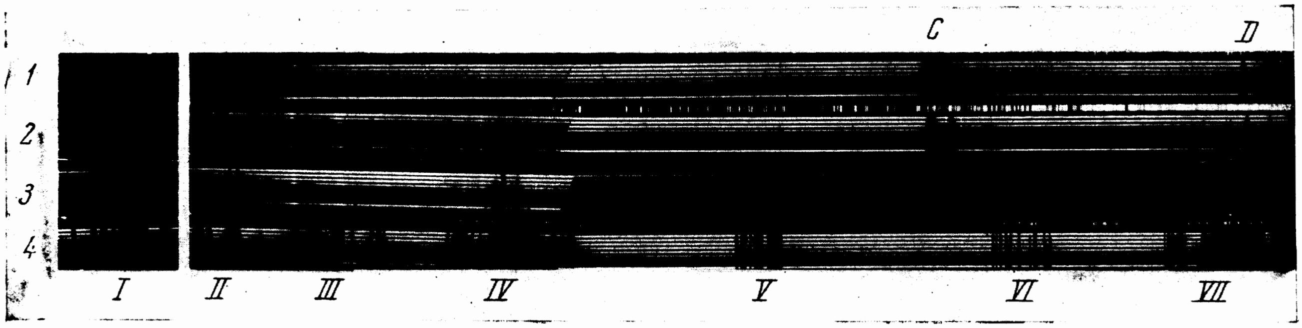

FIG. 1. Absorption spectra of pure MnF_2 and different crystals containing Ho. 1 – MnF_2 (d ~ 1 mm); 2 – MnF_2 + 1% Ho (d ~ 1 mm); 3 – MnF_2 + 1% Ho (d ~ 5 mm); 4 – $Ho_3Al_5O_{12}$ (d ~ 3 mm). The C and D bands of MnF_2 are shown at the top, and the bands I to VII of Ho^{3+} at the bottom. T = 20.4°K

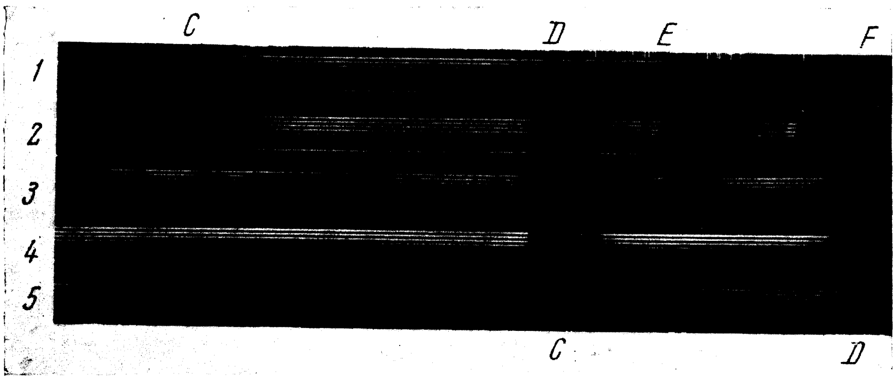

FIG. 2. Absorption spectra of single crystals (d ~ 5–6 mm). 1 – 100% CoF_2; 2 – 90% CoF_2 + 10% MnF_2; 3 – 90% MnF_2 + 10% CoF_2; 4 – 100% MnF_2; 5 – 90% MnF_2 + 10% NiF_2. The CoF_2 bands are shown at the top, and the MnF_2 bands at the bottom. T = 20.4°K.

and 1.36 Å, respectively.[18] In this case an orange mixed crystal was produced. Completely transparent crystals could not be obtained; traces of fault planes of excess impurity were present throughout the entire volume.

2. ABSORPTION SPECTRA OF MIXED CRYSTALS

MnF_2 + 1% Ho. Figure 1 shows the absorption spectra of MnF_2 single crystals, both pure and containing at most 1% Ho, as well as the spectrum of a $Ho_3Al_5O_{12}$ single crystal. A comparison of these spectra leads to the following conclusions:

1. The addition of 1% Ho evidently causes little distortion of the MnF_2 lattice. In any event, the sharpness of the Mn absorption bands and the details of the MnF_2 spectrum remain unchanged, with only a small shift ($\Delta\nu \approx 40$ cm^{-1}) of the entire spectrum to shorter waves.

2. In the spectrum (No. 3) of a MnF_2 + 1% Ho crystal having the thickness d ~ 5 mm at 20.4°K seven groups of narrow absorption bands, assigned to Ho, are observed; the frequencies (ν, cm^{-1}) are given in Table II. The similarity with the spectrum (No. 4) of a $Ho_3Al_5O_{12}$ single crystal and with the spectra of other crystals containing trivalent Ho (Table II) indicates that MnF_2 crystals alloy with trivalent Ho. The frequencies of the observed bands agree satisfactorily with the energy level scheme of Ho^{3+}.[19]

The Ho absorption lines were observed only in the spectrum of MnF_2 + 1% Ho crystals (the second type) that were grown with a small amount of oxygen, which is evidently necessary, as already mentioned, to compensate the excess charge of Ho^{3+}. The spectra of crystals belonging to the second type were reproduced well in many samples. A gradual reduction of sample thickness is accompanied by a regular decrease of Ho^{3+} absorption band intensities. These results indicate a uniform distribution of Ho in very large regions (having linear dimensions of 5 or 6 mm).

$MnF_2(x)CoF_2(1-x)$ and MnF_2 + 10% NiF_2 single crystals. Figure 2 shows the absorption spectra of single crystals of MnF_2, CoF_2, their mixtures, and MnF_2 + 10% NiF_2. The notation of the absorption bands follows that of Finlayson et al.[2] and Balkanski et al.;[5] the band frequencies are given in Table III.

Figure 2 shows that the spectrum of a mixed single crystal comprises the superposition of the spectra of its components; we observe simultaneously the bands of MnF_2 and CoF_2, or of MnF_2 and NiF_2 (which is confirmed by a comparison with the results for pure NiF_2 in[5]). Since the absorption bands of the solvent crystal remain sharp and narrow with a shift of not more than 100 cm^{-1} accompanying a 10% admixture, it can be assumed

Table II

Group of bands	Band No. in group	Band frequency ν, cm^{-1}: Ho spectrum in MnF_2 + 1% Ho crystal	Band frequency ν, cm^{-1}: Ho^{3+} spectrum in different crystals[19]
I	1	18688	18500
	2	18692	
	3	18719	
	4	18735	
	5	18740	
	6	18749	
	7	18764	
	8	18798	
II	1	20743	20600
	2	20764	
	3	20805	20800
III	1	21416	21100
	2	21464	21400
IV	1	22256	22200
	2	22270	
	3	22286	
	4	22316	
	5	22321	
	6	22338	
	7	22370	
	8	22414	
V		24144	24000
VI	1	26076	25800
	2	26125	
VII	1	27763	27700
	2	27797	
	3	27819	
	4	27871	

Table III

Group of Co^{2+} bands	Group of Mn^{2+} bands	Band No. in group	Band frequency ν, cm^{-1}			
			MnF_2	CoF_2	$CoF_2 + 10\%\ MnF_2$	$MnF_2 + 10\%\ CoF_2$
C		1		22773		22500
		2		22903		
		3		23050		
		4		23113		
D		1		25085		
		2		25133		
		3		25202		
		4		25376		
		5		25444		
	C	1	25304		25254	
		2	25398		25398	
		3	25449			
		4	25508			
		5	25559			
		6	25610			
		7	25711			
		8	25762			
		9	25809			
		10	25900			
E		1		26335	26161	26138
		2			26318±20	26406±20
		3			26472±20	26513±20
		4			26730	26750
F		1		28190	28158	
	D	1	27926		27909	
		2	28028			28002
		3	28106			} D_x 28076
		4	28174			
		5	28249			28211
		6	28296			28309
		7	28338			
		8	28367			
		9	28420			28390
		10	28486			28464

that the crystal lattice is distorted only insignificantly with this concentration, as could be assumed from the very similar parameters of all transition-metal fluorides.

The spectrum of a mixed crystal can be regarded as a simple superposition of the spectra of its components only when there is considerable separation of their absorption bands. When the absorption bands of the solvent crystal and the impurity are close, spectral changes are observed (Fig. 2). This applies especially to the spectral region containing the C group of MnF_2 and the E group of CoF_2 bands, or the D group of MnF_2 and the F group of CoF_2. The D group of CoF_2 overlaps the very much more intense C group of MnF_2 and disappears when the concentration 10% MnF_2 is reached.

The behavior of the E band of CoF_2 is the most interesting. In the pure crystal this band is a singlet down to 4.2°K. With the addition of 10% MnF_2 it becomes a quartet of almost equally spaced and equally strong bands. In the MnF_2 + 10% CoF_2 crystal the outside components of the quartet are considerably intensified with practically no frequency shift, while the separation of the central components is reduced almost one-half. In pure MnF_2 and in MnF_2 + 10% NiF_2 no E bands are observed (Fig. 2). The characteristics of the concentration dependence of the E group of CoF_2 resemble somewhat those of the impurity absorption that is spectrally close to the exciton zones observed experimentally in molecular crystals[20,21] and analyzed theoretically in[22]. It is possible that in the case of the $MnF_2(x)CoF_2(1 - x)$ solutions, when the Mn^{2+} and Co^{2+} levels are close, ions of the two different kinds are excited simultaneously, forming mixed common states of both ions and thus causing the unusual behavior of the E band.

We must also discuss the changes in the structure of the D group of MnF_2 following the addition of 10% CoF_2 or 10% NiF_2. In pure MnF_2 this group consists of the strong bands at 28 028 and 28 249 cm^{-1} and the weak (28 106)—(28 174) cm^{-1}

doublet. Upon the addition of 10% CoF_2 or 10% NiF_2 the doublet is replaced by a fairly strong band at 28 076 cm^{-1} (denoted by D_x in Table III). However, while when CoF_2 is added the changed structure of the D group of MnF_2 can be associated with the closeness of the F group of CoF_2, this does not apply when NiF_2 is added. It should also be noted that similar changes of the D-group structure in pure MnF_2 are observed accompanying sublattice investion by a strong external magnetic field ($H_C = 9 \times 10^5$ Oe).[23] The magnetic structure of NiF_2 resembles that of MnF_2 when altered by a strong magnetic field H_C. It is likely that the changes in the D absorption group of MnF_2 accompanying an admixture are associated with a changed magnetic structure of the mixed crystals.

3. INFLUENCE OF ANTIFERROMAGNETIC ORDERING ON IMPURITY ABSORPTION BANDS

Over a broad temperature range we were able to observe only the strongest and narrowest impurity bands: the Ci_1 and E_1 bands of Co^{2+}, the C_1—C_2 doublet of Mn^{2+}, and all seven groups of Ho^{3+}. It was found that for an antiferromagnetically ordered solvent crystal the aforementioned bands of Mn^{2+} and Co^{2+} exhibit anomalies similar to those observed in the absorption spectra of "pure" fluorides. The temperature dependences of the frequencies and half-widths of these Co^{2+} and Mn^{2+} bands are shown in Figs. 3—5, which thus illustrate the following facts:

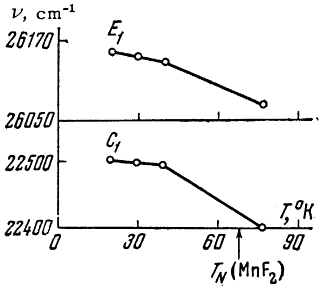

FIG. 3. Temperature dependence of the C_1 and E_1 band frequencies for Co in a MnF_2 + 10% CoF_2 crystal.

1. Magnetic ordering of MnF_2 + 10% CoF_2 crystals ($T_N \approx 70$°K) is accompanied by a large shift of the E_1 and C_1 bands of Co^{2+} to shorter waves. This shift, $\Delta\nu \approx 100$ cm^{-1}, corresponds to the energy kT_N (Fig. 3). These same bands become very much narrower below 70°K.

2. Magnetic ordering of CoF_2 + 10% MnF_2 ($T_N \approx 40$°K) causes a large shift of the C_1 and C_2 bands of Mn^{2+} to shorter waves (Fig. 5) and an anomalous temperature dependence of their half-widths (Fig. 4). The frequency shift $\Delta\nu \approx 75$ cm^{-1} corresponds to the energy kT_N.

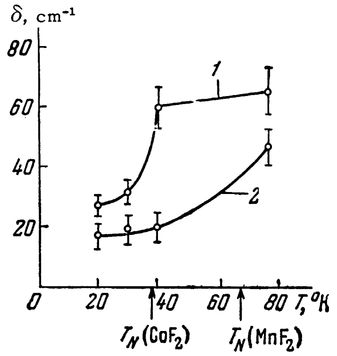

FIG. 4. Temperature dependence of band half-width. 1 – C_1 band of MnF_2 in CoF_2 + 10% MnF_2; 2 – E_1 band of CoF_2 in MnF_2 + 10% CoF_2.

3. The absorption lines of Ho^{3+} are in no way affected by the magnetic ordering of the MnF_2 + 1% Ho crystal. Moreover, the Mn^{2+} bands in this crystal near 70°K exhibit the same characteristics (the frequency shift and narrowing) as in the "pure" crystal (Fig. 6). It can therefore be assumed that 1% Ho does not essentially affect the antiferromagnetic ordering of MnF_2. The fact that the Ho absorption lines are not affected by magnetic ordering indicates a negligibly small exchange interaction of Ho and Mn ions in antiferromagnetic MnF_2. This apparently results from the small radius of the 4f subshell of Ho and its strong screening by external electrons. A similar conclusion for the orthoferrites of rare earths has been based on magnetic measurements.[24]

In conclusion we wish to express our deep appreciation to P. L. Kapitza for his interest, to A. S. Borovik-Romanov for a discussion of the results, and to V. A. Timofeeva for providing the $Ho_3Al_5O_{12}$ single crystals.

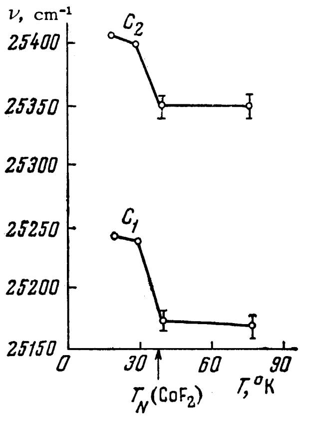

FIG. 5. Temperature dependence of the C_1 – C_2 doublet frequencies for MnF_2 in CoF_2 + 10% MnF_2.

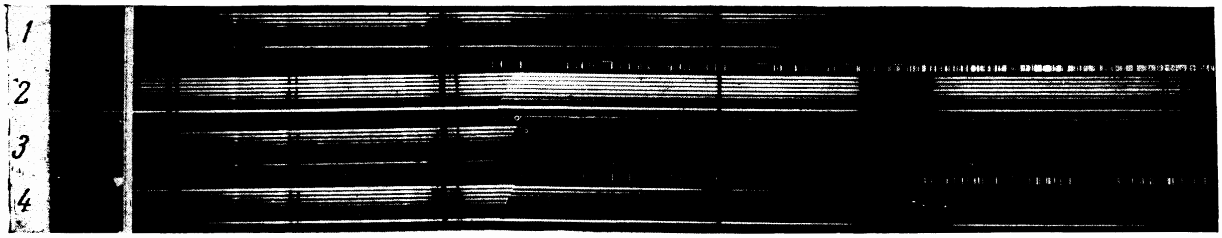

FIG. 6. Absorption spectrum of MnF_2 + 1% Ho single crystal at different temperatures (T°K). 1 – 77°; 2 – 40°; 3 – 20.4°; 4 – 4.2°.

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