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Impurity resonances in $LiY_{1-x}R_xF_4$ compounds

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Several rare-earth-metal impurities (R) are observed in $LiY_{1-x}R_xF_4$ compounds. They are identified by means of magnetic resonance experiments at millimeter and submillimeter wavelengths. Fe^{3+} resonance lines are also observed.

One of the great achievements of the last decade is the understanding of second-order phase transitions via the extensive use of renormalization-group theory. The important prediction that the critical behavior of uniaxial dipolar coupled ferromagnets should obey mean-field theory with logarithmic corrections[1] was first confirmed experimentally in studies on lithium terbium fluoride ($LiTbF_4$).[2,3] Subsequently, Aharony predicted[4] a quite different behavior when some magnetic ions are randomly replaced by nonmagnetic ones. Critical behavior studies[5-7] were performed on $LiTb_xY_{1-x}F_4$.

All these very interesting studies have neglected the presence of unwanted impurities, although it is well known that rare-earth-metal atoms are difficult to separate and impurities are expected. In fact we pointed out in a previous publication the observation of small resonances due to impurities,[8] but impurity resonances do not seem to have been observed in EPR spectra obtained with far-infrared lasers[9,10] in $LiTbF_4$ and $LiHoF_4$.

In this context it is useful to study in more detail the impurity resonances observed in magnetic resonance experiments at millimeter and submillimeter wavelengths. We report here the results obtained on crystalline specimens of lithium yttrium fluoride with terbium or holmium impurities, of lithium terbium fluoride, and of lithium holmium fluoride. The crystals were those used in previous studies[8,11] and some of them had the same origin as those used in Ref. 5. The experiments were carried out in the spectrometer described earlier,[11] at 4.2 K.

Sattler and Nemarich[12] have studied at X-band frequencies the resonances arising from Nd^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+} impurities of concentrations on the order of 1 at. % in single-crystal samples of lithium yttrium fluoride ($LiYF_4$). The spectrum of Tb^{3+} was studied by Laursen and Holmes[13] in the diluted system $LiY_{1-x}Tb_xF_4$ with $x=0.01$, that of Tb^{3+} was studied by Magarino *et al.*[8] in the concentrated system $LiTbF_4$ and that of Ho^{3+} was studied in the diluted system $LiY_{1-x}Ho_xF_4$ by Magarino *et al.*[11] and in the concentrated system $LiHoF_4$ by Magarino *et al.*[8]

As expected in $LiYF_4$ with terbium doping and in $LiTbF_4$, the main resonances arise from Tb^{3+} ions. In the same way, the main resonances in holmium-doped $LiYF_4$ and in $LiHoF_4$ arise from Ho^{3+} ions. The resonance lines arising from impurities are much weaker than those due to the nominally present rare-earth ions but can easily be detected. These impurity lines can be divided into two sets: (i) impurity lines due to rare-earth ions and (ii) impurity lines due to Fe^{3+}.

In $LiYF_4$ with Ho^{3+}, $LiYF_4$ with Tb^{3+}, and $LiHoF_4$, we were able to identify the resonances due to Er^{3+}, Yb^{3+}, and Dy^{3+}. We did not observe the resonance of the Nd^{3+} ions, probably because it is close to that of Fe^{3+} which we describe below.

The spin Hamiltonian which describes the ground-state Kramers doublets of the three ions is:

$$\mathscr{H}=g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B(H_x S_x + H_y S_y) ,$$

where $g_{\parallel}$ and $g_{\perp}$ are the Landé factors for the magnetic field parallel and perpendicular to the c axis, μ_B is the Bohr magneton, and S is the spin.

In addition to the resonances between the levels of the lowest doublets, we observed resonance lines which do not extrapolate to zero energy when the static magnetic field is extrapolated to zero. They correspond to transitions from the levels of the ground-state doublets to excited levels. In Tables I—III we compare our g values to those obtained at the X-band frequency for pure or nearly pure $LiYF_4$ by Sattler and Nemarich indicated by $g_{\parallel}$ (Ref. 12) and $g_{\perp}$ (Ref. 12), and the zero-field energies $\nu(0)$. There are two noticeable differences between the two matrices $LiYF_4$ and $LiHoF_4$. First, for the same transition the Landé factors are slightly different because of different crystal-field parameters. Second, the zero-field energies which extrapolate to zero in $LiYF_4$ extrapolate to positive values in $LiHoF_4$ because of the mean local magnetic field on each ion which arises from the large concentration of magnetic ions in the concentrated system $LiHoF_4$. The resonances shift to lower magnetic field and the zero-field frequencies to positive values. These values differ from sample to sample because of the effect of the demagnetizing field which depends on the shape of the sample (see Table III).

In Tables I and II the $g_{\parallel}$ values for Er^{3+} reported on the first and last rows are different for the lowest and first-excited doublets. Many values of $g_{\perp}$ are not given because it was impossible to follow the corresponding lines in a range of frequencies and fields large enough to enable a precise analysis. Nevertheless, the overall agreement between our millimeter and submillimeter data and the microwave data at the X-band frequency is fairly good

TABLE I. Values of the Landé factors and of the zero-field energies measured in $\mathrm{LiY}_{1-x}\mathrm{Tb}_x\mathrm{F}_4$ with $x=0.02$. The g values are compared to those obtained in LiYF_4 by Sattler and Nemarich (Ref. 12) denoted $g_{\|,\mathrm{SN}}$ and $g_{\perp,\mathrm{SN}}$.

Ion	$g_{\|}$	$g_{\perp}$	$g_{\|,\mathrm{SN}}$	$g_{\perp,\mathrm{SN}}$	$\nu(H=0)$ (GHz)
Er^{3+}	3.02		3.13	8.10	0
Yb^{3+}	1.34		1.33	3.92	0
Dy^{3+}	1.10		1.11	9.22	0
Er^{3+}	3.29				430

TABLE II. Values of the Landé factors and of the zero-field energies measured in $\mathrm{LiY}_{1-x}\mathrm{Ho}_x\mathrm{F}_4$ with $x=0.005$ and 0.02. The g values are compared to those obtained in LiYF_4 by Sattler and Nemarich (Ref. 12) denoted $g_{\|,\mathrm{SN}}$ and $g_{\perp,\mathrm{SN}}$. No significant difference is observed between the samples with $x=0.005$ and those with $x=0.02$.

Ion	$g_{\|}$	$g_{\perp}$	$g_{\|,\mathrm{SN}}$	$g_{\perp,\mathrm{SN}}$	$\nu(H=0)$ (GHz)
Er^{3+}	3.05	8.05	3.13	8.10	0
Yb^{3+}	1.32		1.33	3.92	0
Dy^{3+}		8.85	1.11	9.22	0
Er^{3+}	3.48				435

TABLE III. Values of the Landé factors and of the zero-field energies measured in LiHoF_4. The g values are compared to those obtained in LiYF_4 by Sattler and Nemarich (Ref. 12) denoted $g_{\|,\mathrm{SN}}$ and $g_{\perp,\mathrm{SN}}$.

Ion	Sample number	$g_{\|}$	$g_{\perp}$	$g_{\|,\mathrm{SN}}$	$g_{\perp,\mathrm{SN}}$	$\nu(H=0)$ (GHz)
Er^{3+}	1	2.72		3.13	8.10	20
	2	2.76		3.13	8.10	20
	3	2.90		3.13	8.10	10
Yb^{3+}	1	1.26		1.33	3.92	11
	2			1.33	3.92	
	3	1.31		1.33	3.92	6
Dy^{3+}	1	1.03		1.11	9.22	10
	2	0.95		1.11	9.22	18
	3	1.17		1.11	9.22	5

TABLE IV. Values of the shift ΔH of the resonance $-\frac{1}{2}\rightarrow\frac{1}{2}$ of the Fe^{3+} ions compared to the effective local fields obtained from the shift of Tb^{3+} resonance in LiTbF_4 and of Ho^{3+} in LiHoF_4. The magnetic field is along the c axis.

Host	Sample number	ΔH (kG)	λ_{eff} (kG)
LiTbF_4	1	1.0	1.3
LiHoF_4	1	1.5	1.5
LiHoF_4	2	1.6	1.9
LiHoF_4	3	0.5	0.3

(Tables I and II), as it should be, since the host materials are nearly the same. On the other hand, we report results on the concentrated systems.

Besides the rare-earth-ion resonances, we observed in the three previous hosts and in $LiTbF_4$ very narrow resonances which we attribute to Fe^{3+} ions. Iron impurity ions are known to exist in $LiY_{1-x}R_xF_4$ compounds, but unfortunately the data have not been published.[14]

We have analyzed the resonances using the appropriate effective spin Hamiltonian[15] corresponding to the S_4 tetragonal symmetry of the scheelite structure. The ground state of Fe^{3+} is $^6S_{5/2}$ ($L=0$, $S=5/2$). As expected, we found $g=1.993\pm0.015$, a value very close to the value of the free ion $g=2.0023$.

In the host matrices $LiTbF_4$ and $LiHoF_4$, the Fe^{3+} resonances are shifted from their positions in $LiYF_4$. We have studied this shift on the $-\frac{1}{2}\rightarrow\frac{1}{2}$ transition and compared it with the effective molecular field λ_{eff} obtained for the main lines[8] (arising from the concentrated rare-earth ions), taking into account the demagnetizing factor. The comparison is shown in Table IV. The agreement is very good.

In summary, we have analyzed the resonance lines arising from impurities in nominally pure $LiY_{1-x}R_xF_4$ compounds, either diluted or concentrated. The impurity resonances reported here were not observed in laser experiments,[9,10] probably because of the lower resolution which can be obtained in such experiments.

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