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Ligand electron-nuclear double resonance of ^{19}F ions around Yb^{3+} impurities in fluorites

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Results of electron-nuclear double-resonance experiments performed on four shells of fluorine nuclei surrounding Yb^{3+} impurities at cubic sites in the four fluorite lattices CdF_2, CaF_2, SrF_2, and BaF_2 are reported. The data are described in terms of a Hamiltonian for the transferred hyperfine interactions (THFI) including an anisotropic nuclear Zeeman term. The contribution of the dipole-dipole magnetic interaction A_d is analyzed for different coordination spheres using calculated values for the impurity-ligand distance. These are obtained from a model for the local distortions around trivalent rare-earth impurities. The covalent contributions to the THFI constants are important for nearest neighbors, and a comparison of the values determined for Yb^{3+} is made with a similar set for the isoelectronic $(4f^{13})$ Tm^{2+} ions in the same lattices.

I. INTRODUCTION

The transferred hyperfine interaction (THFI) of rare-earth impurities with neighboring ions is dominated by dipole-dipole magnetic interactions in the case of distant ligands. For nearest neighbors the experimental values for the THFI parameters cannot be explained solely by this interaction, as covalent contributions arising from the admixture of the rare-earth orbitals with those of the ligands become important.

The case of the isoelectronic ions Yb^{3+} and Tm^{2+} in fluorites constitute a very interesting system to study these effects since their electronic structure is comparatively simple: The configuration of lowest energy for both ions has a partially filled shell $4f^{13}$, i.e., a single hole in the otherwise closed $4f$ electronic shell.

For Tm^{2+} there is a considerable amount of experimental data concerning the THFI interaction. The covalent part of the interaction, obtained after subtraction of the calculated dipolar contribution, has been studied[1,2] as a function of the impurity-ligand distance R in different lattices. The simple functional dependence observed (proportional to R^{-n} with $n \sim 12$) seemed to confirm that a simple mechanism was responsible for the THFI interaction. Baker[3] has explained the parameters measured for Tm^{2+} and Yb^{3+} in CaF_2 assuming that this mechanism is the direct covalency between the $4f$ electron and ligand orbitals, as originally proposed by Axe and Burns.[4] In this model, differences between the THFI parameters for Tm^{2+} and Yb^{3+} arise from changes in the overlap integrals due to the different ion-ligand distances and radial extent of the electron wave functions for divalent and trivalent rare-earth ions.

However, recent calculations by Anikeenok *et al.*[5] indicate that direct overlap is not the only effective mechanism, since charge transfer to empty shells of the rare-earth ion, and processes of excitations of the outer $5p$ electrons into the $4f$ shell with simultaneous transfer of the ligand electron to the emptied $5p$ orbital, also make important contributions. For these mechanisms an important role is played by the structure of energy levels of the ions, this being in this model the main reason for differences between Tm^{2+} and Yb^{3+}.

A third contribution must also be considered:[6] The changes in the covalency due to the electric polarization of the ligands. This electric polarization is always present around impurities, due to the reduction of the symmetry of ligand sites, but it is expected that it will be larger around trivalent rare-earth impurities due to their extra charge with respect to the metal ions they replace.[7]

As in the case of divalent thulium, we considered that a detailed study of the dependence of the THFI parameters on the impurity-ligand distance R for the case of trivalent ytterbium in different fluorites could help to clarify the relative importance of the contributions from different mechanisms. In this paper we report results obtained for the THFI parameters corresponding to four shells of fluorine nuclei around Yb^{3+} impurities in cubic sites of the four fluorite lattices CdF_2, CaF_2, SrF_2, and BaF_2. In Sec. II we present our ENDOR (electron-nuclear double-resonance) results and analyze the experimental data in terms of appropriate effective spin Hamiltonians. In Sec. III we discuss the effects of local distortions, both radial and angular, on the dipole-dipole magnetic contribution to the THFI parameters for distant fluorine neighbors. For nearest neighbors the dependence of the covalent part of the THFI parameters on the impurity-ligand distance is analyzed and a comparison with the corresponding behavior of Tm^{2+} is made. The contribution of different theoretical mechanisms proposed is discussed. Finally the shifts of the ^{19}F nuclear gyromagnetic factors with respect to the free nucleus are briefly discussed.

II. EXPERIMENTAL RESULTS

The samples used, single crystals of MeF_2 fluorites with Me=Cd, Ca, Sr, and Ba, nominally doped with 0.05 mol % YbF_3, were supplied by Optovac, Inc. The Yb^{3+}

TABLE I. Yb^{3+} ligand-ENDOR parameters for nearest-neighbor F$^-$ ions in fluorite lattices. Values for A_s, A_p, A_d, and A_p' are given in MHz.

	CdF$_2$	CaF$_2$	SrF$_2$	PbF$_2$	BaF$_2$
R^a (Å)	2.2820	2.2907	2.3194	2.3183	2.3478
g_s	5.2509(15)	5.2507(15)	5.2509(15)		5.2508(15)
g_p	0.0030(5)	0.0026(3)	0.0031(9)		0.0030(8)
A_s	1.692(6) 1.5^c	1.809(4) 1.80^d 1.667(10)^e 1.67(5)^f	1.407(10)	1.378(30)^b	1.059(8)
A_p	17.884(5) 18.2^c	17.636(3) 17.625^c 17.567(10)^c 17.57(5)^f	16.628(10)	16.386(30)^f	15.834(9)
δg_s (calc.)	0.0004	0.0004	0.0003		0.0003
g_p (calc.)	0.0038	0.0038	0.0040		0.0042
A_d	10.720	10.614	10.219	10.216	9.847
A_p'	7.164	7.022	6.409	6.170	5.987

[a] Reference 7.

[b] Reference 14.

[c] Te-Tse Chang, M. I. Cohen, and W. R. Hosler, J. Chem. Phys. **54**, 4278 (1971).

[d] Reference 11.

[e] Reference 12.

[f] Reference 13.

ions occupy substitutionally metal sites of the host having cubic point symmetry. The extra charge of the Yb^{3+} ions requires a compensating F$^-$ ion which sometimes occupies a site nearby, distorting the symmetry of the rare-earth environment. In fact, cubic as well as tetragonal or trigonal sites are identified in the electron paramagnetic resonance spectra. The EPR spectrum for the Yb^{3+} isotopes with nuclear spin $I=0$ in cubic sites consists of a single isotropic line corresponding to electronic transition within a Γ_7 ground doublet.[8,9] Ligand-ENDOR spectra were identified for the four nearest coordination spheres of fluorine ions around the Yb^{2+} impurities and their resonant frequencies fitted to appropriate spin Hamiltonians. It is worth mentioning that although the number of cubic sites is greatly reduced in going from CdF$_2$ to BaF$_2$ we have found in all cases adequate signal-to-noise ratios for their ENDOR spectra. All the experiments were carried out in a Q-band (35 GHz) spectrometer[10] at liquid-helium temperatures.

A. Nearest-neighbors

The THFI between the rare-earth impurity and its nearest fluorine ligands is usually characterized by a Hamiltonian with axial symmetry having two parameters:[8,9] A_s and A_p. When fitting our data to this Hamiltonian the residuals had a mean value of about 25 kHz, which is beyond the uncertainty of the measurements, showing also a systematic deviation when plotted against the angle between the ligand axis and the magnetic field. These residuals were reduced to about 8 kHz with the inclusion of an anisotropic pseudonuclear Zeeman interaction term.[8] This need for additional terms proportional to the magnetic field has also been found in the fitting of NMR spectra[11] of ligand fluorine nuclei for Yb^{3+} in CaF$_2$. The ENDOR Hamiltonian used is

$$\mathcal{H}=\mathcal{H}_0+g_e\mu_B\mathbf{H}\cdot\mathbf{S}-g_s\mu_N\mathbf{H}\cdot\mathbf{I}-g_p\mu_N(3H_zI_z-\mathbf{H}\cdot\mathbf{I})$$
$$+A_s\mathbf{S}\cdot\mathbf{I}+A_p(3S_zI_z-\mathbf{S}\cdot\mathbf{I})\ , \qquad (1)$$

where $\mathcal{H}_0$ describes the electronic degrees of freedom. The results from the least-squares fit of the data taken with the magnetic field oriented parallel to the crystalline directions [001], [110], [111], and [112] are given in Table I. In the case of Yb^{3+}: CaF$_2$ three previous experiments have been reported. Our results are in good agreement with the NMR data obtained in Ref. 11; however, we cannot explain the differences with the other reported values,[12,13] obtained from ENDOR experiments at 9 GHz.

B. THFI with second F$^-$ neighbors

The ENDOR Hamiltonian we used to describe the spectra of nearest neighbors has the axial symmetry appropriate for the C_{3v} symmetry of the site. The point symmetry of second neighbors is C_{1h} and the THFI Hamiltonian reflects this lower symmetry having five adjust-

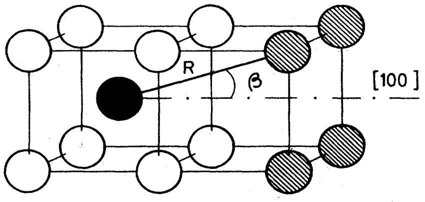

FIG. 1. Nearest neighbors (open circles) and next-nearest neighbors (shaded circles) to the paramagnetic impurity (solid circles) in the fluorite lattice.

TABLE II. Yb^{3+} ligand-ENDOR parameters for next-nearest neighbor F^- ions in fluorites. Values for A_s, A_p, B_1, and B_2+B_3 are given in MHz.

	CdF_2	CaF_2	SrF_2	PbF_2	BaF_2
g_s	5.2520(15)	5.2521(15)	5.2530(15)		5.2541(15)
g_p	0.0005(2)				
g_p (calc.)	0.0003	0.0003	0.0003		0.0003
A_s	0.017(3)	0.023(8) 0.015(5)[b]	0.007(6)	0.029(10)[a]	−0.002(8)
A_p	1.461(2)	1.417(6) 1.418(5)[a]	1.192(4)	1.138(10)[b]	0.985(10)
B_1	−0.002(6)	−0.018(14)	−0.009(10)		−0.018(19)
B_2+B_3	0.006(7)	0.000(7)	0.005(18)		−0.003(19)

[a] Reference 14.
[b] Reference 12.

able parameters:[15]

$$\mathscr{H}=-g_s\mu_N\mathbf{H}\cdot\mathbf{I}-g_p\mu_N(3H_zI_z-\mathbf{H}\cdot\mathbf{I})+A_s\mathbf{S}\cdot\mathbf{I}+A_p(3S_zI_z-\mathbf{S}\cdot\mathbf{I})+B_1S_xI_x+B_2S_xI_z+B_3S_zI_x\ , \tag{2}$$

where the z axis is taken parallel to the impurity-fluorine bond; see Fig. 1. As in Ref. 15, we have limited the least-squares fit to four parameters: A_s, A_p, B_1, and B_2+B_3 because the contribution of B_2-B_3 to the measured ENDOR frequencies is smaller than the experimental resolution. The results are given in Table II.

C. More distant neighbors

Lines corresponding to fluorine ions in the third- and fourth-coordination spheres have also been identified in the ENDOR spectra. These lines are correctly described in terms of a Hamiltonian with axial symmetry as it is expected for nearly pure dipole-dipole magnetic interaction and the parameters obtained are given in Table III. In order to check for covalent contributions we added an isotropic term to the THFI Hamiltonian. The resulting values for A_s always overlapped zero within the estimated errors, and no significant improvement of the fit was observed.

III. DISCUSSION

A. Dipolar interaction and distortion of the lattice

The almost purely dipolar origin of the THFI for the third and fourth fluorine coordination spheres in the cubic centers, suggested by the axial symmetry of the spectra, was confirmed by comparison of the measured values of A_p with those calculated for the dipolar contribution A_d:

TABLE III. Yb^{3+} ligand-ENDOR parameters for the third and fourth F^- coordination spheres. $A_d(R_0)$ and $A_d(R)$ are calculated values for the dipolar THFI for F^- ions at distances R_0 and R, these being the values for the perfect and distorted lattice, respectively. Values for A_p and A_d are given in MHz.

Coordination sphere	Parameter	CdF_2	CaF_2	SrF_2	PbF_2	BaF_2
III	g	5.2521(15)	5.2526(15)	5.2527(15)		5.2543(15)
	A_p	0.637(6)	0.611(6) 0.622(5)[b]	0.518(9)	0.485(5)[a]	0.428(6)
	$A_d(R_0)$	0.638	0.611	0.511	0.479	0.418
	$A_d(R)$	0.640	0.613	0.517	0.494	0.428
IV	g	5.2524(15)	5.2530(15)	5.2545[c]		5.2550(15)
	A_p	0.376(9)	0.362(4) 0.362(5)[b]	0.311[c]	0.284(5)[a]	0.249(7)
	$A_d(R_0)$	0.377	0.360	0.301	0.283	0.247
	$A_d(R)$	0.378	0.362	0.302	0.284	0.248
Pure lattice	g[d]	5.2544	5.2549	5.2550		5.2554

[a] Reference 14.
[b] Reference 12.
[c] Standard deviations have not been estimated because only two lines of the spectrum have been clearly identified, along [111].
[d] Reference 17.

TABLE IV. Yb^{3+} ligand-ENDOR parameters for next-nearest-neighbor F^- ions assuming only axial interactions. Values for A_s, A_p, and A_d are given in MHz.

	CdF_2	CaF_2	SrF_2	BaF_2
g_s	5.2520(15)	5.2523(15)	5.2530(15)	5.2542(15)
g_p	0.0005(2)	(0.0003)	(0.0003)	(0.0003)
A_s	0.017(3)	0.017(6)	0.003(5)	−0.012(10)
A_p	1.461(3)	1.420(7)	1.192(6)	0.985(14)
$\Delta\beta$	0.20(8)°	0.20(30)°	0.28(26)°	0.41(63)°
$A_d(R_0)$	1.449	1.387	1.159	0.948
$A_d(R)$	1.462	1.405	1.182	0.970
$\Delta\beta$ (calc.)	0.17°	0.21°	0.28°	0.35°

$$A_d = g_e g_F \mu_B \mu_N / R^3 ,$$

where R is the distance between the Yb^{3+} ions and the F^- nuclei. These are not exactly equal to the distances in the pure crystals since the lattices are locally distorted around the impurities.[2,7] Although small, the corrections for these distant neighbors are not completely negligible: This effect is clearly noticed in PbF_2, SrF_2, and BaF_2 (see Table III), where the difference between the ionic radii of the Yb^{3+} ions and the metal ions they replace is largest.

For second F^- neighbors we have considered the possibility of radial and angular distortions, ΔR and $\Delta\beta$, which are allowed while preserving the cubic symmetry of the Yb^{3+} sites; see Fig. 1. These angular distortions would make an axially symmetric Hamiltonian appear as one of lower symmetry of the type given by Eq. (2), if referred to the crystalline undistorted bonding axis. Baker and Wood[15] have suggested that this may be the case for Gd^{3+} impurities in PbF_2, indicating an angular distortion of 0.5(2)°.

In an effort to obtain experimental evidence of these angular distortions in the case of Yb^{3+} impurities we have fitted the experimental data using an axial Hamiltonian, leaving the orientation of the bonding axis as an adjustable parameter. The values so obtained are given in Table IV, where the angular distortion ranges from 0.2° to 0.4°. These results led us to modify our model for calculating local distortions around trivalent rare-earth impurities[7] in order to allow for the angular displacements which are given in Table IV. These are very close to the values we obtained from ENDOR data and show the same systematic increase in going from CdF_2 and CaF_2 to BaF_2.

B. Covalent contributions to the THFI parameters

The covalent contribution to the THFI parameters for nearest neighbors has been estimated by subtracting from the measured values the calculated dipolar interaction using the impurity-ligand distances R, calculated in Ref. 7. The resulting parameters for Yb^{3+} in cubic sites A_s and $A_p' = A_p - A_d$ are listed in Table I and a comparison with the corresponding values for the isoelectronic ion Tm^{2+} is made in Fig. 2, as a function of R, using the values given in Ref. 2.

In the case of A_s the values for Yb^{3+} are significantly smaller than those expected by extrapolation from the Tm^{2+} values, but they are larger for A_p'. The direct covalency model[3,4,16] depends only on the admixture of the rare-earth $4f$ orbitals with the $2s$ and $2p$ orbitals of the ligand fluorine and it would be difficult to explain the observed behavior solely by differences in the radial extent of the $4f$ wave functions in divalent and trivalent rare-earth ions. On the other hand, the charge transfer mechanism proposed by Anikeenok *et al.*[5] explains, according to their calculation, the increase of A_p' for Yb^{3+} based on the differences in the structure of energy levels of Yb^{3+} and Tm^{2+}. For A_s the expected net contribution of the two mechanisms is very similar for both ions[5] and the decrease observed is probably due to effects of the electric polarization of fluorine ions. In fact, an estimate[6] of the contribution of this mechanism indicates a reduction of both A_s and A_p' of about 60% and 20%, respectively.

C. ^{19}F gyromagnetic factor in crystal lattices

The g values measured for distant $^{19}F^-$ ligands reflect the chemical shifts found for pure fluorite lattices.[17] For nearer neighbors an additional contribution is important: the so-called pseudonuclear Zeeman interaction[8] that gives contributions proportional to the THFI constants A_s and A_p,

$$\delta g_s = k A_s , \quad g_p = k A_p ,$$

where $k = 2g_J(\mu_B/\mu_N)/[E(\Gamma_8) - E(\Gamma_7)]$. The values for

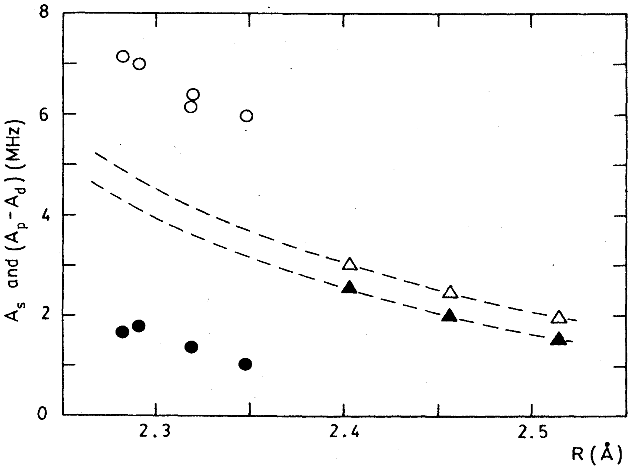

FIG. 2. Covalent contributions to the THFI constants vs the calculated ligand-impurity distance R for Tm^{2+} (triangles) and Yb^{3+} (circles) on cubic sites. Solid and open symbols correspond to A_s and A_p', respectively.

δg_s and g_p calculated from the measured THFI parameters for nearest neighbors are given in Table I. We have used for the energy difference between crystal-field levels $E(\Gamma_8)-E(\Gamma_7)$, values extrapolated[18] from CaF_2. The differences between calculated and measured values are probably due to the anisotropy in the chemical shifts arising from the presence of the rare-earth ion.[19] For the next-nearest neighbors g_p has been estimated from the ENDOR spectrum in the case of CdF_2. The values obtained are consistent with the pseudonuclear Zeeman interaction calculated from the measured A_p. The contribution of this term to the measured frequencies amounts only to about 5 kHz, very close to the limit of the experimental resolution. For the other lattices calculated values of g_p have been used in the analysis of the spectra, in order to reduce the number of unknown parameters to be determined from the experimental data. All values are given in Table II.

The g values measured for distant fluorine ligands are given in Table III, together with those corresponding to the pure lattice, which have been calculated from chemical-shift data.[17] Both sets of data show the same systematic behavior in going from CdF_2 to BaF_2, although there are differences in the numeric values slightly beyond the estimated experimental errors.

IV. CONCLUSIONS

From our ENDOR data we have determined the axial contribution A_p to the THFI for third and fourth fluorine neighbors around Yb^{3+} impurities, finding excellent agreement with the values predicted for the dipolar interaction when taking into account the local distortions of the lattice.[7] For second neighbors our measurements confirm the existence of an angular distortion of the lattice as proposed by Baker.[15] Our model for calculating distortions[2] was modified to allow for this kind of distortion obtaining again good agreement with the experimental results.

For nearest neighbors we have determined the covalent contribution to the THFI by subtracting the dipolar part, estimated from the calculated-distance fluorine impurity. Although our experimental results do not contradict the predictions of existing calculations,[5,6] any serious attempt to quantitatively explain the THFI parameters should take into account the delicate balance of the contributions arising from the mechanisms involved. The detailed dependence of A_s and A_p' with the impurity-ligand distance is a characteristic that may help to understand this balance. As shown in Ref. 2 both parameters have a similar dependence for Tm^{2+} ions, i.e., proportional to R^{-n} with $n \approx 12$. For Yb^{3+} instead, we have found that A_s and A_p' have a significantly different behavior: $n \approx 21$ for A_s and $n \approx 7$ for A_p'. To our knowledge there are no estimates of the expected R dependence of the different mechanisms proposed, and it would be of interest to compare these predictions, when available, with the observed dependence of the THFI parameters.

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[18] Values for the energy differences between crystal field levels for Yb^{3+} in fluorites have been extrapolated from the values given in Ref. 9 for the crystal-field parameters of Yb^{3+} in CaF_2. For the extrapolation we have assumed the same functional dependence on the impurity-ligand distance determined for the isoelectronic Tm^{2+} in the same lattices.

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