

Short Notes

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EPR Investigation of New Electron-Excess Centres in LiF:Co

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Introduction Hayes and Wilkens discovered a number of paramagnetic defects in LiF:Na, namely centres I to VII and A to G, respectively (hereafter notations of [1] are used). They ascribed these centres to different states of the Jahn-Teller ion Ni⁺.

In our previous paper [2] centres VI, VII, and Co⁺ in LiF:Co were investigated. It was shown that centres VI, VII have a hole nature and are molecular ions F₆⁵⁻. This note concerns the centres IV, V.

Experimental details Crystals of LiF:Co were grown from the melt by the Stockbarger method in a helium atmosphere. The impurity concentration determined by spectral analysis was 0.25 wt%. The samples were X-irradiated for 1 h with the tube operating at 40 kV and 50 mA. The spectra were recorded at room temperature (RT).

Results The centres are observed after X-irradiation at RT. Centres IV and V appear and are destroyed always together and have relative intensities of 2:1, respectively. The data on the centres are presented in Fig. 1 and 2 and Table 1.

For **B** || <100> quintets with an intensity distribution of 1:4:6:4:1 and greatly overlapping septets with a distribution of 1:2:3:4:3:2:1 are observed. The septets are converted by rotating the crystal in a magnetic field into nonets with a distribution of 1:2:1:2:4:2:1:2:1.

Centres IV, V are destroyed in the range from 60 to 200 °C.

Discussion and conclusions Hayes and Wilkens explained the absence of HFS caused by nickel by the small amount of ⁶¹Ni (1.13%, *I* = 3/2), but the substitution ^{58,60,62,64}Ni (98.87%, *I* = 0) → ⁵⁹Co (100%, *I* = 7/2) in our experiments did not change the spectra markedly.

Table 1

Parameters of spectra of centres IV and V. Data for LiF:Ni are taken from [1]. HF constants are expressed in MHz. The errors were ±0.001 and ±3 MHz for *g* and *A*, respectively

centre	LiF:Co				LiF:Ni				
	<i>g</i>	<i>g</i> _⊥	<i>A</i>	<i>A</i> _⊥	<i>g</i>	<i>g</i> _⊥	<i>A</i> _x	<i>A</i> _y	<i>A</i> _z
IV	2.553	2.096	109.3	252.9	2.541	2.096	254.8	121.4	113.0
V	2.540	2.104	103.4	222.3	2.528	2.096	254.8	121.4	113.0

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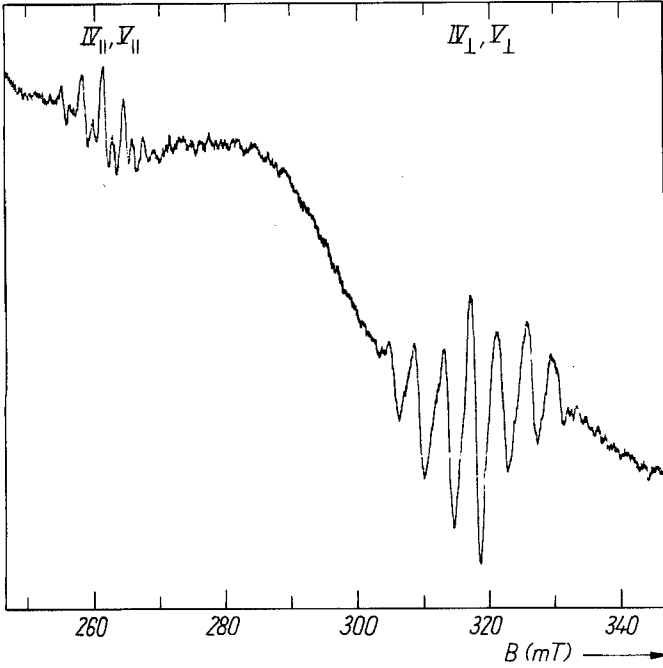


Fig. 1. EPR spectrum of LiF:Co after X-irradiation at RT. Recording temperature is RT, $B \parallel \langle 100 \rangle$, $\nu = 9.3309$ GHz

The resemblance of spectra IV, V in LiF:Co to those in LiF:Ni might be explained by the isoelectronicity of Ni^{+} and Co^0 , but the different charges of the central ions lead to a different HFS of the fluorines. In spite of that practically the same HFS is observed and HFS due to the Co nucleus is absent. Obviously the unpaired electron of the defect does not belong to the impurity ion. In analyzing these centres we are using a spin-Hamiltonian

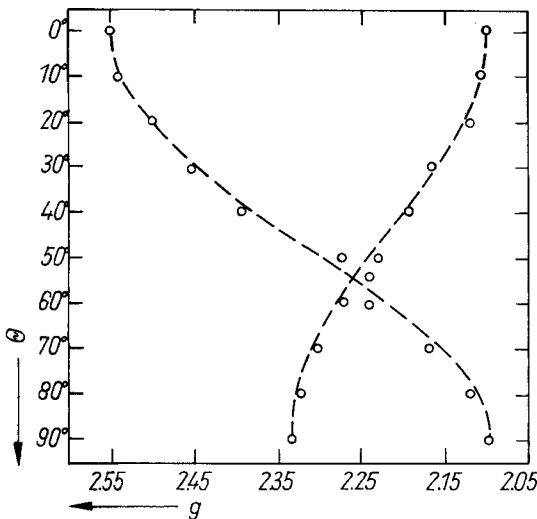


Fig. 2. Angular dependence for the centre IV in LiF:Co, $g = g(\theta)$. Rotation around $\langle 110 \rangle$; \circ are experimental values; --- theoretical curves; θ angle between magnetic field B and $\langle 100 \rangle$. The two curves correspond to parallel ($g_{\parallel} = 2.553$) and perpendicular ($g_{\perp} = 2.096$) spectra

(SH) in the form:

$$\frac{\mathcal{H}}{g_0 \mu_B} = \frac{1}{g_0} \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{i=1}^4 \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}_i, \quad (1)$$

where the sum corresponds to the four fluorine nuclei. The theoretical curve corresponding to the axial symmetry was calculated according to the expression

$$g^2(\theta) = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \quad (2)$$

for Fig. 2 where g_{\parallel} , g_{\perp} were taken from the spectrum for $\mathbf{B} \parallel \langle 100 \rangle$. The principal axes of the \mathbf{g} -tensor are $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$. The centres have tetragonal symmetry.

The quintet of the parallel spectrum can be explained by the interaction of the unpaired electron with the four equivalent nuclei of fluorine, then the perpendicular spectrum must give a nonet due to two pairs of equivalent nuclei of fluorine, but a septet is observed because of the casual equation $A_{\parallel} = 2A_{\perp}$.

We think that when growing the crystal, part of the impurity enters the matrix in bivalent form compensated by the nearest cation vacancy, which after X-irradiation becomes the geometrical centre of defects IV, V.

A model of the defects is presented in Fig. 3. The electron cloud of the centre is oriented along the symmetry axis connecting two anion vacancies. The similar parameters of SH of the centres IV, V in LiF:Co and LiF:Ni indicate the weak influence of the impurity, which is probably in monovalent form. We consider the centres IV and V as the same centre so explaining the difference between the spectra by the different angles which the magnetic field \mathbf{B} makes with the bonding directions. At $\mathbf{B} \parallel \langle 100 \rangle$ for centre IV, $\alpha = 45^\circ$, and for centre V, $\beta = 90^\circ$ (Fig. 3). Thus the relative intensities of 2:1 are explained statistically.

Some formation and destruction processes in LiF:Co, LiF:Ni, and NaF:Ni It is possible to group some centres observed in these crystals according to their g -factors and HF constants: centres VI, VII, D, "F" form the first group, I to V, A, B, C, E form the second one.

Analysis of annealing curves in Fig. 5 to 7 of [1] leads to the following: (i) when V_K -centres are destroyed the centres VI, D are formed, therefore we can ascribe the latter to the hole type; (ii) destruction of V_K -centres and centres I, A occurs simultaneously and we can

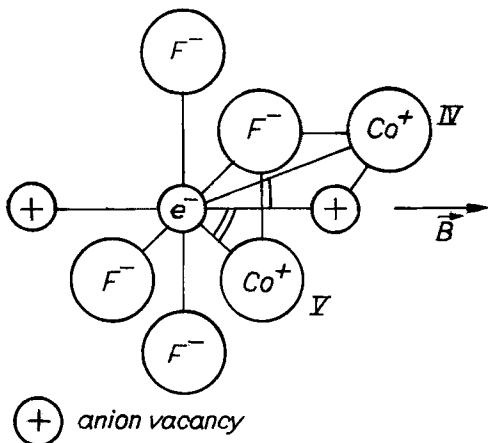


Fig. 3. Model of centres IV and V in LiF:Co. The impurity ion occupies either IV or V position

suppose recombination and attribute the latter to the electron-excess type; (iii) taking into consideration the following conversion, namely $I \rightarrow II \rightarrow III$, $A \rightarrow C$, $VI \rightarrow VII$, $D \rightarrow \text{“F”}$ it is reasonable to ascribe the centres II, III, C to the electron-excess type and centres VII, “F” to the hole type.

Centres formed under X-irradiation at RT, namely IV, V, VII and E, “F” are destroyed at rising temperature practically simultaneously (Fig. 5 to 7 of [1], Fig. 2 of [2]). Since the centres VII and “F” have hole nature, it is reasonable to suppose recombination with electron-excess centres IV, V, and E, respectively.

It is very likely that the centres I to V, A, B, C, E are the same electron-excess centre, and small differences of SH parameters are caused by interaction with different hole centres of the V-type as well as with diamagnetic centres (for example with X_3^- -centres). Also centres VI, VII, D, “F” are probably the same hole centre, which interacts with centres F and some diamagnetic electron-excess centres.

Obviously the different thermal stability of the centres I to V, A, B, C, E is caused by the different mobility of vacancies at different temperatures as well as by recombination with different centres at these temperatures. The same conclusion can be drawn concerning the centres VI, VII, D, “F”.

Note also that the formation and destruction processes of centres G [1] and Co^+ [2] are similar, and, taking into account $g = 2.332$ of G close to the values of $3d^9$ ions, it is possible to attribute the centre G to an aggregate of Ni^+ ions.

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