

EPR STUDY OF IMPURITY CENTRES IN NATURAL CaF₂

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The EPR method (X-band) was chosen for the identification of impurity ions in a natural single crystal of CaF₂ from Cumberland, England. The presence of Gd³⁺ and Eu²⁺ ions in the EPR spectra of the CaF₂ single crystal was proved as a result of the best fitting procedure. The following values for crystal field parameters were obtained: For Gd³⁺, $g = 1.992$, $B_2^0 = 0.77729 \times 10^{-4} \text{ cm}^{-1}$, $B_4^0 = 0.000008 \times 10^{-4} \text{ cm}^{-1}$, $\Delta E = 0.14916 \text{ cm}^{-1}$. For Eu²⁺, $g = 1.993$, $B_2^0 = 0.91649 \times 10^{-4} \text{ cm}^{-1}$, $B_4^0 = -0.000006 \times 10^{-4} \text{ cm}^{-1}$, $\Delta E = 0.08707 \text{ cm}^{-1}$, $^{151}\text{A} = 36.0 \text{ cm}^{-1}$, $^{153}\text{A} = 15.1 \text{ cm}^{-1}$.

ИЗУЧЕНИЕ ЦЕНТРОВ ПРИМЕСЕЙ В ПРИРОДНОМ CaF₂ С ПОМОЩЬЮ МЕТОДА ЭПР

Для идентификации ионов примесей в природном монокристалле CaF₂, полученном из Камберленда (Англия), был выбран метод ЭПР (X-диапазон). Присутствие Gd³⁺ и Eu²⁺ в ЭПР-спектрах монокристалла CaF₂ доказано на основе метода наилучшей подгонки. Для параметров внутркристаллического поля были получены следующие значения: для Gd³⁺, $g = 1.992$, $B_2^0 = 0.77729 \cdot 10^{-4} \text{ см}^{-1}$, $B_4^0 = 0.000008 \cdot 10^{-4} \text{ см}^{-1}$, $\Delta E = 0.14916 \text{ см}^{-1}$. Для Eu²⁺: $g = 1.993$, $B_2^0 = 0.91649 \cdot 10^{-4} \text{ см}^{-1}$, $B_4^0 = -0.000006 \cdot 10^{-4} \text{ см}^{-1}$, $\Delta E = 0.08707 \text{ см}^{-1}$, $^{151}\text{A} = 36,0 \text{ см}^{-1}$, $^{153}\text{A} = 15,1 \text{ см}^{-1}$.

1. INTRODUCTION

Models of paramagnetic centres are suggested on the basis of an analysis of EPR spectra and its angular dependence. All spectra were obtained at room temperatures. The suitability of the models was examined by numeric analysis on a digital computer SIEMENS 4004/150 at the Computing Centre of the Comenius University.

The results indicate that the symmetries of the sites occupied by the Gd³⁺ and Eu²⁺ ions remain cubic. A great many data are available in literature, concerning the iron group and rare earth group ions, both built into synthetic CaF₂ single crystals [1—6] belonging to the O_h space group, exhibiting cubic [7, 8], tetragonal

[9—11] or trigonal [12—14] symmetries of the F⁻ ion site. Ca²⁺ ions occupy the sites situated in the centres of the next-neighbour cells.

This paper presents the results of measurements and analyses of the EPR spectra of two impurity ions, namely Gd³⁺ and Eu²⁺. The electron configuration of the trivalent Gd ion is 4f⁷, the ground orbital singlet state ⁸S_{7/2}; the total electron spin of the ion being $S = 7/2$ and the nuclear spin $I = 3/2$. All data are valid for both ¹⁵⁵Gd and ¹⁵⁷Gd isotopes. The electron configuration of the divalent Eu ion is 5f⁷, with the ground state ⁸S_{7/2}, which also is an orbital singlet. The total electron spin $S = 7/2$ and the nuclear spin $I = 5/2$ for both natural isotopes ¹⁵¹Eu and ¹⁵³Eu.

II. CALCULATION

We succeeded in calculating the energy levels of both Gd³⁺ and Eu²⁺ ions from a Hamiltonian of the following form [4]: $\hat{H}_i = g\beta H_0 \hat{S}_i + B_0(\hat{O}_2^0 + 5\hat{O}_4^0) + B_2(\hat{O}_2^0 - 21\hat{O}_4^0) + \mathcal{A}\hat{S}_i$, where we use these symbols: \hat{O}_i^m equivalent operators of the crystal field, \mathcal{A} tensor of a hyperfine structure, H_0 vector of the dc magnetic field, B_i^m crystal field parameters, \hat{S}_i operator of the total electron spin, \hat{I} operator of the nuclear spin, g spectroscopic splitting factor, β Bohr magneton.

Three different programs were used in order to obtain the best agreement between the measured and calculated positions of the spectral lines and their amplitudes. The first program was used for the best fitting of the crystal field parameters B_i^m and it was a modified version of the Kalavský and Patraš [15] program. The second, according to [16], was used for the direct calculation of the position of the fine structure spectral lines, as well as of transition probabilities and hyperfine spectral line positions. The last, third program [17] yields the angular dependence of EPR fine structure spectral line positions.

III. EXPERIMENT

The probe crystal was fixed along the direction [0, 0, 1] so that the dc magnetic field vector rotated within the (0, 0, 1) plane when the angular dependences of spectra were measured. Let us note here that the natural cleavage plane of the CaF₂ single crystal is the (1, 1, 1) plane.

Positions of the centres of spectral lines were measured by means of the proton resonance.

III.1. Gadolinium

The whole EPR spectra of the examined crystal exhibits several tens of spectral lines. However, seven of these lines were distinguishable at first sight because of

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their amplitudes and their symmetric arrangement with respect to the main, biggest line. The main line corresponds to the transition between the $-1/2$ and $+1/2$ electron spin states of Gd^{3+} , the separation between the seven lines being proportional to $16:10:8:1:8:10:17$. The zero field energy splitting due to the crystal field as the LS coupling is $\Delta E = 0.14916 \text{ cm}^{-1}$, which is the value corresponding to the ion in the S -state. The ground state which was originally an orbital singlet with an eightfold electron spin degeneracy has been split by the cubic environment of the ion into a doublet, a quartet and another doublet. The corresponding crystal field parameters are: $g = 1.992$, $B_2^0 = 0.77729 \times 10^{-4} \text{ cm}^{-1}$, $B_4^0 = 0.00008 \times 10^{-4} \text{ cm}^{-1}$, $B_2^{-2} = 3.88645 \times 10^{-4} \text{ cm}^{-1}$, $B_4^{-2} = -0.00173 \times 10^{-4} \text{ cm}^{-1}$. The calculated relative intensities of the spectral lines in fine structure spectra may be expressed as $7:15:12:16:12:15:7$, the corresponding transition among the electron spin states being $-7/2:3/2:5/2:1/2:-5/2:-3/2:7/2$, respectively. The experiment yields the following intensities of spectral lines: $1.5:5:4:16:4:11:1.5$. The discrepancy between the measured and calculated values of the intensities is not surprising. A similar discrepancy was reported in [16] and it seems to be due to the fact that the Russell—Saunders approximation was used in both cases, which is not the best for ions in the S -ground state [19—22].

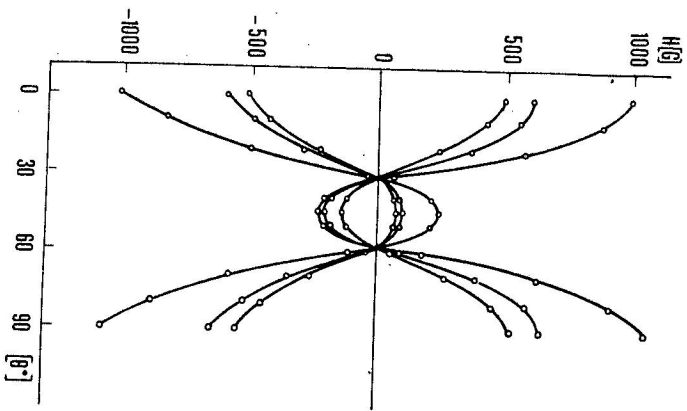


Fig. 1. The angular dependence of EPR spectra of $CaF_2:Gd^{3+}$.

Table 1

Transition	The position of fine spectral lines			
	Gd^{3+} calculated	Eu^{2+}	Gd^{3+} exp.	Eu^{2+}
$-7/2$	$-5/2$	2105		2107
$5/2$	$7/2$	2280	2283	
$-5/2$	$-3/2$	2543		2541
$3/2$	$5/2$	2660	2658	
$-3/2$	$-1/2$	2682		2686
$1/2$	$3/2$	2770	2766	
$-1/2$	$1/2$	3250		3251
$-1/2$	$1/2$	3258	3254	
$-3/2$	$-1/2$	3773	3773	
$1/2$	$3/2$	3858		3859
$-5/2$	$-3/2$	3865	3865	
$3/2$	$5/2$	3972		3972
$-7/2$	$-5/2$	4280	4280	
$5/2$	$7/2$	4458		4461

The results of the angular dependence of EPR spectra are plotted in Fig. 1. The excellent agreement between the calculated and measured spectral line positions is seen also in Tab. 1. This agreement was the very argument which led us to the conclusion that one of the impurity ions in the natural CaF_2 single crystal was Gd^{3+} .

III.2. Europium

The zero field splitting due to the crystalline field and the LS coupling yields the values $\Delta E = 0.08707 \text{ cm}^{-1}$, $g = 1.993$, $B_2^0 = 4.58245 \times 10^{-4} \text{ cm}^{-1}$, $B_4^0 = 0.00126 \times 10^{-4} \text{ cm}^{-1}$ for the second impurity ion. In Tab. 1 there are presented the values of line positions calculated by means of the computer, these values being compared with the measured line positions in the EPR spectra, for all the seven lines of the fine structure of Eu^{2+} . The agreement is very good. But in the case of the Eu^{2+} ion we have one proof more for its presence in the crystal. It is the well distinguished hyperfine structure presented in Tab. 2. The position of the hyperfine spectral lines were computed and measured from the EPR spectra, exhibiting a good agreement between theory and experiment. The corresponding hyperfine structure constants are: $^{151}A = 36.0$, $^{153}A = 16.1$ in 10^4 cm^{-1} for the two natural isotopes of ^{151}Eu and ^{153}Eu , respectively.

4006	3995.8	4475.1	4482.1
4023	4028.8	4492	4498.3
4072	4068.9	4515	4512.9
		4563	4551.1

IV. CONCLUSION

The best fitting procedure in the calculation of the crystal field parameters B_n^m and B_n^m of Gd^{3+} and Eu^{2+} was performed with standard deviation parameters $K = 0.39192 \times 10^{-4} \text{ cm}^{-1}$ and $K = 0.66053 \times 10^{-4} \text{ cm}^{-1}$, respectively. The best fit values fulfill the condition $B_4^0 \gg B_6^0$, proving that the environment has a nearly cubic symmetry for the sites occupied by both ions. The angular dependence of the EPR spectra in Fig. 1 can serve as the third argument confirming the identification of the impurity ions was correct. All spectral lines diminished to zero at the angles $\Theta = 32^\circ$ and 58° , when the dc magnetic field vector was rotated in the (1, 0, 0) plane of the crystal.

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REFERENCES

- [1] Alšuler S. A., Kozyrev N. V., *Elektronnyj paramagnitnyj rezonans*. Izdat. Nauka, Moskva 1972.
- [2] Orton J. W., *Electron Paramagnetic Resonance*. London ILLFEE books Ltd. 1968.
- [3] Weber M. J., Bierig R. W., *Phys. Rev. A* **134** (1964), 1492.
- [4] Baker J. M., Bleaney B., Hayes W., *Proc. Roy. Soc. A* **247** (1958), 141.
- [5] Low W., *Paramagnetic Resonance in Solids*. *Sol. Stat. Phys. Suppl.* **2**. Academic Press, New York—London 1960. Translation into Russian III. Moskva 1962.
- [6] Abragam A., Bleaney B., *Electron Paramagnetic Resonance Of Transition Ions*. Clarendon Press, Oxford 1970.
- [7] Low W., *Phys. Rev.* **109** (1958), 265.
- [8] Ryter Ch., *Helv. Phys. Acta* **XXX** (1957), 353.
- [9] Sierrro J., *Helv. Phys. Acta* **36** (1964), 505.
- [10] Vinokurov V. M., Zaripov M. M., Poliskij J. E., Stepanov V. G., Čirkin G. K., Šekun L. J., *Fiz. tver. tela* **4** (1962), 2238.

- [11] Sierrro J., *Lacroix R., Compl. Rend.* **250** (1960), 2686.
- [12] Vinokurov V. M., Zaripov M. M., Poliskij J. E., Stepanov B. G., Čirkin G. K., Šekun L. J., *Fiz. tver. tela* **5** (1963), 599.
- [13] Sierrro J., *J. Chem. Phys.* **34** (1961), 2183.
- [14] Sierrro J., *Phys. Letters* **4** (1963), 178.
- [15] Kalavský S., Patráš M., *to be published*.
- [16] Uher L. T., *Czech. J. Phys. B* **25** (1975), 331.
- [17] Macák K., Belluš M. D., *Proc. of the 3rd Conf. of Czechoslovak Physicists*. Olomouc 1974.
- [18] Manenkov A. A., Poliskij J. E., *ŽETF* **45** (1963), 1425.
- [19] Sandars P. G. H., Beck J., *Proc. Roy. Soc. A* **289** (1955), 97.
- [20] Sharma R. R., Das T. P., *Phys. Rev.* **149** (1966), 257.
- [21] Sharma R. R., Das T. P., *Phys. Rev.* **155** (1967), 338.
- [22] Sharma R. R., Das T. P., *Phys. Rev.* **171** (1968), 378.

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