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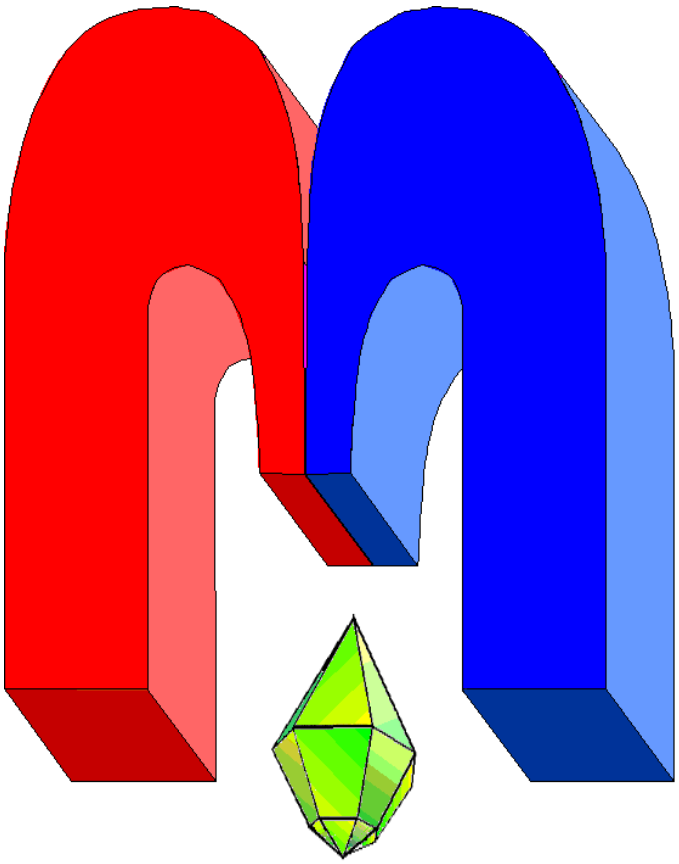

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* Address: "Magnetic Resonance in Solids. Electronic Journal", Kazan Federal University; Kremlevskaya str., 18; Kazan 420008, Russia
† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.
‡ Dedicated to Professor Boris Z. Malkin on the occasion of his 85th birthday

High-frequency EPR of Fe^{2+} ion in the $CsCdBr_3$ crystal†

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In $CsCdBr_3$ crystals, the EPR spectra of Fe^{2+} ion replacing Cd^{2+} ion in a trigonally distorted octahedron were recorded and studied in the subterahertz frequency range. The zero-field splitting parameter and the value of the g-factor are determined. A comparative analysis of the obtained experimental results with literature data is made.

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1. Introduction

EPR spectroscopy of the ground state of the Fe^{2+} ion in various compounds is currently represented by only a small number of works. This is due both to the traditional difficulty of studying non-Kramers ions and to the peculiarities of the formation of the fine structure of divalent iron. The energy intervals between low-laying electronic states are in the subterahertz and terahertz range, where there are still problems with suitable radiation sources. Standard EPR spectrometers do not have sufficient quantum magnitude to detect resonant transitions between low-lying states. If the ground state turns out to be a non-Kramers doublet, then resonant transitions are often prohibited by selection rules. At the same time, the relevance of such research is dictated by the enormous role that Fe^{2+} ions play in physics, biology, medicine and technology. In particular, it is known that, thanks to Fe^{2+} ions, hemoglobin carries oxygen in the blood. Divalent iron is involved in the process of photosynthesis and is part of metalloproteins. Fe^{2+} ion ion is associated with the coloring of some precious gems (aquamarine, peridot) and the operation of efficient IR lasers (ZnSe:Fe). The presence of Fe^{2+} determines the magnetic properties of many materials used in technology.

This paper presents the results of studying the EPR spectra of divalent iron in the subterahertz frequency range in a $CsCdBr_3$ crystal. Previously, the study of this crystal with impurities of rare earth ions was carried out in Kazan under the guidance of KFU professor B.Z. Malkin. A series of works was published on this topic [1–5], in which crystal fields were calculated and the Stark structure of single and pair centers was determined. The calculations were based on optical spectra and EPR. Measurements of some crystals were carried out using high-frequency EPR spectroscopy [4, 5]. It was found that the excitation spectrum of all samples contained a line from an uncontrolled impurity. Analysis of experimental results and the literature data showed that it belongs to the Fe^{2+} ion. Thus, this article is an addition to previously done research, and it is dedicated to the 85th anniversary of prof. B.Z. Malkin.

The $CsCdBr_3$ crystal has hexagonal symmetry (space group $P6_3\,mmc$). Cd^{2+} ions are localized in trigonally distorted octahedra that have common faces and form quasi-one-dimensional chains. A structural analogue of bromide, a $CsMgCl_3$ crystal with impurities of iron group ions, was previously intensively studied by EPR. It was found that transition ions replace cadmium,

†This paper is dedicated to Professor Boris Z. Malkin, who made a significant contribution to the field of magnetic radio spectroscopy in Kazan University, on the occasion of his 85th birthday.

and in the case of trivalent ions, for example Cr^{3+} , predominantly pair centers are formed in the crystal. The formation of dimers is explained by the condition of charge conservation during doping. Three Cd^{2+} ions located along the quasi-one-dimensional chain are replaced by two Cr^{3+} ions separated by a cadmium vacancy [6]. For divalent cations, there are no conditions for the formation of dimers and divalent iron ions replace cadmium with local symmetry D_{3d}.

The $CsCdBr_3$:Fe^{2+} crystal was previously investigated as part of a comprehensive study of compounds of the AMX_3 type. (A = Cs, Rb, Tl, $(CH_3)_4N$; M = Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Cd; X = Cl, Br, I) by Raman scattering and Mössbauer spectroscopy methods [7]. One of the results of this study was the establishment of energy intervals between low-lying states of the $^5T_{2g}$ multiplet of the Fe^{2+} ion in the $CsCdBr_3$:Fe^{2+} crystal. The values of the energy gap between the ground and first excited levels given in this work are in good agreement with the results of the present work. Due to high-frequency EPR spectroscopy method, the accuracy of the measurement was significantly increased and, besides, the g-factor of the Fe^{2+} ion was determined. For a concentrated system, i.e. in the $CsFeBr_3$ crystal, there is a phase transition to the antiferromagnetic state at temperature $T = 17\,\mathrm{K}$. In the paramagnetic phase, the $CsFeBr_3$ crystal was studied using high-frequency ESR spectroscopy [8]. Although a large number of resonant transitions were observed, the authors concluded that there is no complete understanding of the experimental data. Thus, studying the EPR spectra of a dilute crystal will contribute to a more complete understanding of the processes in a concentrated system.

2. Experimental details and results

The measurements were carried out at the temperature of liquid helium on a homemade EPR spectrometer [9]. The operating range of the spectrometer has been expanded through the use of additional backward wave generators and is currently in the range of 1.3–28 cm^{-1}. The crystals ($CsCdBr_3$:Nd^{3+}, $CsCdBr_3$:Ho^{3+}, $CsCdBr_3$:Tm^{3+}) were grown at the Technical University of Darmstadt (Germany). A detailed description of growth is given in [10]. EPR lines of Fe^{2+} ion were observed in the frequency range 585–625 GHz.

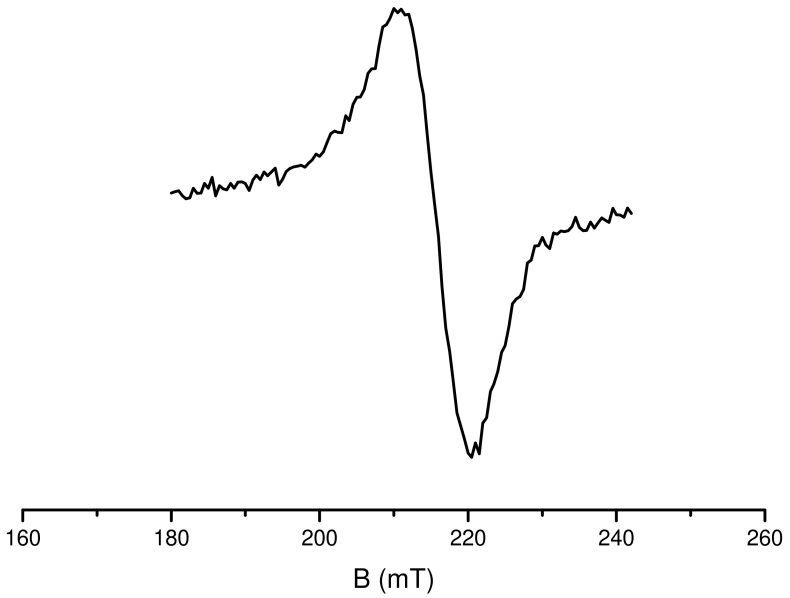

Figure 1. EPR spectra of the Fe^{2+} ion in $CsCdBr_3$ crystal. The orientation of the magnetic field is along the trigonal axis. ($\nu = 600.6\,\mathrm{GHz}$, $T = 4.2\,\mathrm{K}$).

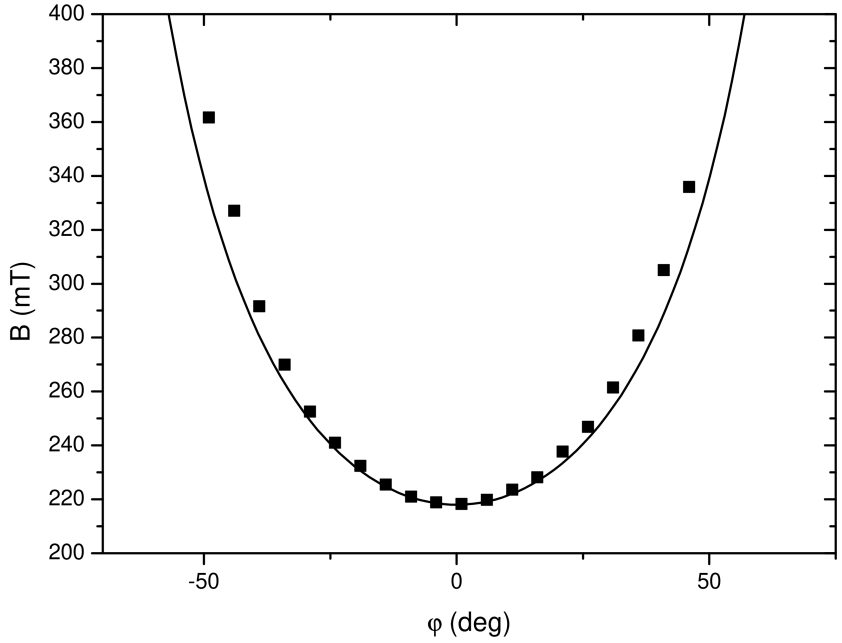

Figure 2. Angular dependence of the resonant magnetic field in $\{11\bar{2}0\}$ plane at frequency of 600 GHz of the EPR signal of Fe^{2+} ions in crystal $CsCdBr_3$. Black squares and solid line represent, respectively, the experimental data and its approximation by the function $B(\varphi) = B(\varphi_0)/\cos\varphi$, where $\varphi_0 = 0$.

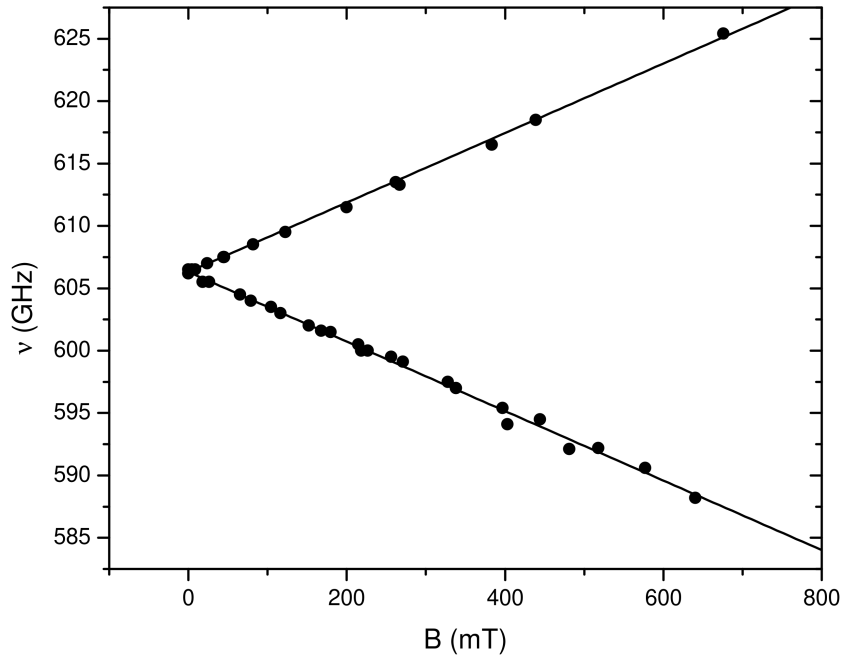

Figure 3. Field dependence of the resonant transition frequency of Fe^{2+} ions in $CsCdBr_3$ crystal. The orientation of the magnetic field is along the trigonal axis. Circles and solid lines represent the experimental data and the calculation, respectively.

Figure 1 shows the EPR spectrum of the Fe^{2+} ion in the crystal $CsCdBr_3$:Nd^{3+} for the orientation of the magnetic field along the trigonal axis. For crystals with holmium and thulium impurities, the lines were of the same order in intensity and width. The angular dependence of the EPR spectrum measured at the frequency of 600 GHz with crystal rotation in the $\{11\bar{2}0\}$

plane is presented in Figure 2. The absence of lines from magnetically nonequivalent positions and the direction of the maximum g-factor along the trigonal axis indicates an isovalent substitution of the Fe^{2+} ion for the Cd^{2+} ion. Figure 3 shows the frequency-field dependence of the EPR spectra for the magnetic field directed along the trigonal axis, which in our case is the direction of the parallel g-factor. There are two branches with a linear dependence of the frequency of resonant transitions on the magnetic field. From this graph we can conclude that resonant transitions of the singlet-doublet type are observed. The magnitude of the splitting in zero field (606.3 GHz) was measured by the direct method with an accuracy of 0.5 GHz. To describe a system of three energy levels, the following spin Hamiltonian with effective spin $S = 1$ was used:

$$H = g_{\parallel}\mu_{\mathrm{B}}B_zS_z + g_{\perp}\mu_{\mathrm{B}}(B_xS_x + B_yS_y) + D(S_z^2 - S(S+1)/3). \quad (1)$$

Fitting the experimental points of the frequency-field dependence gave the following parameter values $D = 606.3$ GHz, $g_{\parallel} = 1.99$. The inverse cosine function (Figure 2), which we used to describe the angular dependence, in high magnetic fields gave a mismatch between the calculation and experiment. To improve agreement with the experiment, it is necessary to take into account the influence of the perpendicular g-factor. However, as the angle between the trigonal axis and the magnetic field increased, the EPR lines quickly broadened and the signal-to-noise ratio decreased. So, an attempt to extract the value of the perpendicular g-factor from the angular dependence was unsuccessful due to large errors in determining the position of the EPR line.

3. Discussion

The incorporation of divalent iron into a trigonally distorted octahedron was previously detected using thermal phonons in corundum. The zero-field splitting (ZFS) between the ground singlet and the excited doublet was ZFS = 112.5 GHz, and the measured g-factor value was $g = 3.5$ [11]. In the $YAlO_3$:Fe crystal, EPR signals were also recorded due to resonant transitions between the main singlet and the excited doublet (ZFS = 215.2 GHz, $g = 2.02$) [12], but the identity of this center with the Fe^{2+} ion was not firmly established. A detailed analysis of the EPR spectra in a trigonally distorted octahedron was performed for a $CaCO_3$:Fe^{2+} crystal [13], but in this work the main energy level was a non-Kramers doublet, the g-factor of which was $g = 9.85$. A similar result was obtained by the acoustic EPR method for the $Y_3Al_5O_{12}$:Fe^{2+} crystal where divalent iron occupied an octahedral position [14]. The change in the symmetry of the ground state is associated with a different sign of the axial field. In our case, the sign of the trigonal field parameter is positive. Using the notation from [7], the symmetry of the ground and excited states is γ_1 and γ_3, respectively. The work [13] presents the calculated dependence of the doublet g-factor and the dependence of the distance between the singlet and doublet levels on the magnitude and sign of the parameter of the trigonal component of the crystal field. For the ZFS value of 20.2 cm^{-1} that we measured, the calculated value of the trigonal component is in the range of 300–500 cm^{-1}. Accordingly, the calculated g-factor takes a value of about $g \sim 4$. This is consistent with our data and serves as additional confirmation of the identification of the spectra.

Acknowledgments

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