Electron Nuclear Double Resonance of the Cubic Dy$^{3+}$ Center in the KZnF$_3$ Single Crystal

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Abstract. ENDOR measurements on the $^{19}$F nuclei in the first four shells of KZnF$_3$ containing Dy$^{3+}$ ions in the cubic site are reported. The values and signs of the hyperfine and transferred hyperfine interaction parameters are determined. The local deformation of the crystal lattice in the vicinity of the impurity ion is estimated. The theoretical analysis of the THFI parameters for the first coordination shell of the F$^-$ ions has been carried out. For the Dy$^{3+}$ ion the influence of spin polarization of the closed 5s and 5p shells is considered for the first time. Spin polarization is shown to play a significant role in the mechanisms of rare-earth ion-ligand coupling.

1. Introduction

Crystals of the perovskite type ABF$_3$ (A = K$^+$, B = Mg$^{2+}$, Zn$^{2+}$) are promising materials for practical applications and good model systems for the corroboration and the development of the theory of the electron-nuclear interaction between impurity rare-earth ions (IREI) and the magnetic moments of ion-ligands of the nearest environment (transferred hyperfine interaction – THFI). The theory developed in [1–5] enabled us to take into account in a simple way the contribution to THFI due to polarization of the 5s and 5p shells of IREI not only for the S-state ions (4f$^7$ – Gd$^{3+}$, Eu$^{2+}$), but, for the first time, also for other configurations as well (4f$^{11}$ – Er$^{3+}$ [4, 6], 4f$^{13}$ – Yb$^{3+}$ [6, 7]). An important aspect in the theoretical description of the experimental results of THFI is the determination of the actual distances between the IREI and the ligands. These problems were studied in this work where the experimental and theoretical study of THFI of the cubic centre Dy$^{3+}$ in a single crystal KZnF$_3$ was carried out. Previously we have studied THFI of Dy$^{3+}$ in KMgF$_3$ [8]. This investigation cannot be considered as complete because of insufficient experimental data (due to the absence of the signals from the $^{19}$F nuclei of the dis-
tant coordination shells it was impossible to estimate the distance between Dy$^{3+}$ and F$^-$, and the absence, at that time, of a method for taking into account the polarization contribution to THFI for the 4f$^9$-configuration. An attempt to solve these deficiencies is presented in this paper where the new analysis of THFI for Dy$^{3+}$ in KMgF$_3$ is carried out as well.

2. Experimental

KZnF$_3$:Dy$^{3+}$ single crystals were grown by the Czochralski method under an atmosphere of helium. Dysprosium was inserted into the melt as DyF$_3$. EPR and ENDOR spectra were recorded at $T = 4.2$ K on a home built EPR and ENDOR spectrometer based on an E 110 Varian X-band equipment and on an ERS-231 spectrometer modified by adjoining an ENDOR attachment.

The EPR spectrum of the cubic center of the even Dy$^{3+}$ isotope is shown in Fig. 1 where the hyperfine structure components of the $^{161}$Dy$^{3+}$ and $^{163}$Dy$^{3+}$ isotopes are also marked. The EPR parameters of the studied center and the analogous data for KMgF$_3$ (from [9]) are given in Table 1. The ENDOR experiments were for the most part carried out on the even Dy$^{3+}$ isotope. In contrast to KMgF$_3$:Dy$^{3+}$ the ENDOR lines from F$^-$ nuclei forming four nearest coordination shells were observed. In order to establish exactly the correspondence between the lines and the respective fluorine nuclei the angular dependence of the ENDOR spectra in the (001) plane was studied. Spectra pertaining to the first fluorine coordination shell and their plot of the angular dependence are shown in Figs. 2 and 3, respectively. These latter results allow one to establish that firstly the Dy$^{3+}$ is situated at the center of a regular octahedron, e.g., it substitutes for a Zn$^{2+}$, and secondly that the compensation

![Fig. 1. The EPR spectrum of KZnF$_3$:Dy$^{3+}$. $T = 4.2$ K, $\nu = 9.251$ GHz.](image-url)