ISSN 2072-5981
doi: 10.26907/mrsej

Volume ***21***
Special Issue ***4***
Paper No ***19401***
1-3 pages
2019
doi: **10.26907/mrsej-19401**

http://mrsej.kpfu.ru
http://mrsej.ksu.ru

Established and published by Kazan University
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140),
August 2, 1996
First Issue appeared on July 25, 1997

© Kazan Federal University (KFU)*

"***Magnetic Resonance in Solids. Electronic Journal***" (**MRSej**) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (*ESCI*, Clarivate Analytics, from 2015),
Scopus (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*,
DOAJ, *ROAD*, *CyberLeninka* (from 2006), *SCImago Journal & Country Rank*, etc.

Editor-in-Chief
Boris **Kochelaev** (KFU, Kazan)

Honorary Editors
Jean **Jeener** (Universite Libre de Bruxelles, Brussels)
Raymond **Orbach** (University of California, Riverside)

Executive Editor
Yurii **Proshin** (KFU, Kazan)
mrsej@kpfu.ru

Editors
Vadim **Atsarkin** (Institute of Radio Engineering and Electronics, Moscow)
Yurij **Bunkov** (CNRS, Grenoble)
Mikhail **Eremin** (KFU, Kazan)
David **Fushman** (University of Maryland, College Park)
Hugo **Keller** (University of Zürich, Zürich)
Yoshio **Kitaoka** (Osaka University, Osaka)
Boris **Malkin** (KFU, Kazan)
Alexander **Shengelaya** (Tbilisi State University, Tbilisi)
Jörg **Sichelschmidt** (Max Planck Institute for Chemical Physics of Solids, Dresden)
Haruhiko **Suzuki** (Kanazawa University, Kanazava)
Murat **Tagirov** (KFU, Kazan)
Dmitrii **Tayurskii** (KFU, Kazan)
Valentine **Zhikharev** (KNRTU, Kazan)

Special Editor of Issue
Eduard **Baibekov** (KFU)

Technical Editors of Issue
Nurbulat **Abishev** (KFU)
Maxim **Avdeev** (KFU)
Eduard **Baibekov** (KFU)
Alexander **Kutuzov** (KFU)

This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License.

This is an open access journal which means that all content is freely available without charge to the user or his/her institution. This is in accordance with the BOAI definition of open access.

---

* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Short cite this: *Magn. Reson. Solids* **21**, 19401 (2019) doi: 10.26907/mrsej-19401

EPR of single Yb^{3+} ions in $CsCdBr_3$ monocrystals

L.K. Aminov*, M.R. Gafurov, I.N. Kurkin, S.I. Nikitin, A.A. Rodionov
Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia
**E-mail: Linar.Aminov@kpfu.ru*

(Received May 26, 2019; accepted May 28, 2019; published June 6, 2019)

New measurements of EPR spectra in single crystals $CsCdBr_3$:Yb^{3+} are presented. The lines due to pairs of Yb^{3+} ions and single Yb^{3+} ions are observed. The spectra indicate the existence of several types of single Yb^{3+} paramagnetic centers. Resolved superhyperfine structure of some lines of these centers is observed for the first time.

PACS: 76.70.Dx, 75.10.Dg, 61.43.Bn.
Keywords: EPR, rare-earth, crystal.

On the occasion of the 80th anniversary of B.Z. Malkin

1. Introduction

The substantial part of the scientific activity of Prof. B.Z. Malkin is devoted to the investigations of the structure of the admixture paramagnetic centers in crystals. He developed an effective model of exchange charges in the theory of crystal fields and worked out the comprehensive programs for simulation of optical and EPR spectra. These studies are extensively employed for the interpretation of very diverse experimental results. From applications to real systems, in the present report we shall dwell on the system $CsCdBr_3$:Yb^{3+} which was already studied by a number of researchers, among them B.Z. Malkin (see [1] and cited there papers).

Besides applications in laser techniques this crystal is interesting due to the pronounced dimeric structure of paramagnetic centers. The crystal is composed of linear chains of Cd atoms stretched along the third order axis. Each atom is surrounded by an octahedron of six Br atoms, the neighboring octahedrons having a common face. The [$CdBr_3$] chains are bounded through the chains of Cs atoms disposed between them. Already the first investigations show that trivalent paramagnetic ions in double bromide crystals form charge compensated dimers of the RE^{3+}-vacancy – RE^{3+} type which substitutes for three successive Cd^{2+} ions in a chain. EPR spectra of such centers are explained rather satisfactorily with taking into account magnetic dipole – dipole and weak antiferromagnetic interactions between admixture ions. The fact that RE ions in double bromides form not only the pair centers was for the first time clearly demonstrated in Ref. [1] just in the crystal $CsCdBr_3$:Yb^{3+}. Besides EPR spectra of dimers, the authors observe EPR lines definitely belonging to the single Yb^{3+} ions. At the same time a number of other curious circumstances were found, that is, the variation of the relative concentration of dimers and single ions within the same single crystal and the irregular dependence of the relative concentration on general concentration of ytterbium ions in a sample. All this indicate that further investigations of the considered system are necessary. In this report we present some new measurements of EPR spectra for the system $CsCdBr_3$:Yb^{3+}. They indicate to the existence of several types of single Yb^{3+} centers. For the first time in this system superhyperfine structure of some EPR lines was revealed.

2. Experimental results

$CsCdBr_3$ single crystals doped with Yb^{3+} ions were grown by the Bridgman method in quartz sealed ampoule by lowering in the furnace with temperature gradient of about 60°C/cm with rate of about 0.5 mm/h. CsBr (Merck, Germany, 99.99% purity), $CdBr_2$ (Merck, Germany, 99.99%

purity), and YbBr$_3$ (Cerac, USA, 99.99% purity) bromides were used as starting materials. The concentration of Yb^{3+} ions in the starting materials were varied from 0.1 to 1 at. % of substituted Cd^{2+}. The quality of the crystals were tested by optical methods and X-ray diffraction. Six samples were investigated with nominal concentration of ytterbium ions within 0.1 – 1.0 at. %. The EPR measurements were made at X-band (microwave frequency ν is about 9.42 GHz) *cw* Bruker ESP 300 spectrometer at low temperatures, typically at $T = 10$ K. The low temperature measurements were made using the Oxford Instruments ESR 9 helium flow cryogenic system.

In a sample with the highest concentration (1.0 at. %) of paramagnetic centers only intensive EPR spectrum of the symmetric Yb^{3+}–Yb^{3+} dimer is observed. In other samples supplementary lines of different intensity appear, which may be ascribed to axial paramagnetic centers with single Yb^{3+} ion. One may separate out at least three such centers.

In Fig. 1 EPR spectra of the sample with the greatest content of single ions are presented for $\mathbf{B} \parallel \mathbf{c}$ and $\mathbf{B} \perp \mathbf{c}$. By D the lines due to dimeric D-center are designated. A, B, C correspond to three different single-ion centers, the A-center being discussed before in [1]. The measured concentrations of paramagnetic centers in this sample (compared with the reference point CaF$_2$: 0.8 at. % Er) are the next: A-centers – 0.068, B-centers – 0.011, C-centers – 0.004, D-centers – 0.1 at. %. g-factors of single ions are the following: A: $g_{||} = 3.33$, $g_{\perp} = 2.16$; B: $g_{||} = 3.449$, $g_{\perp} = 2.082$; C: $g_{||} = 3.16$, $g_{\perp} = 2.219$.

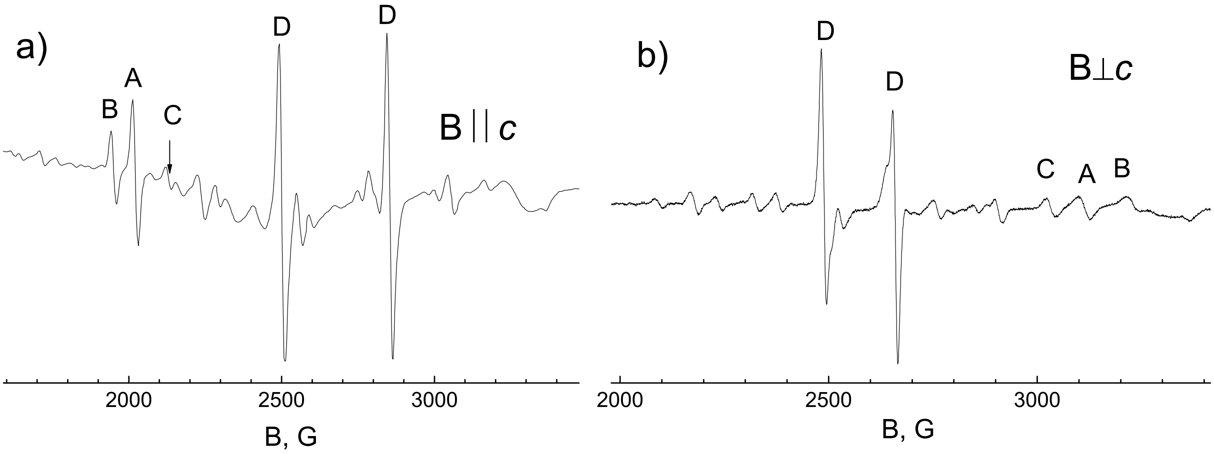

Figure 1. EPR spectra of Yb^{3+} ions in CsCdBr$_3$ single crystal. a) $\mathbf{B} \parallel \mathbf{c}$; b) $\mathbf{B} \perp \mathbf{c}$, $\nu = 9.417$ GHz, $T = 10\,$K. A, B, C refer to single Yb^{3+} ions; D refer to Yb^{3+}–Yb^{3+} dimer.

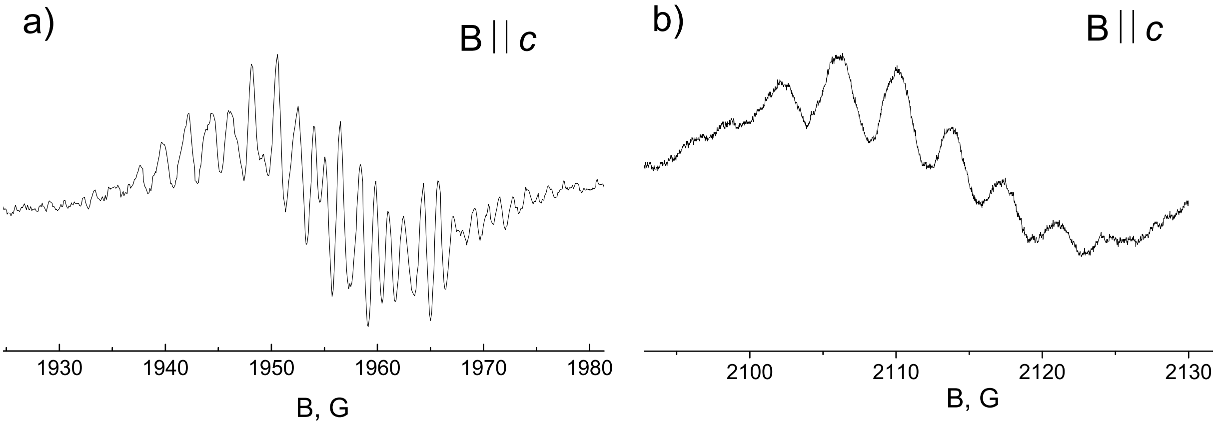

Figure 2. Superhyperfine structure of EPR spectra of single Yb^{3+} in CsCdBr$_3$. a) B-center, b) C-center. $\mathbf{B} \parallel \mathbf{c}$, $\nu = 9.417\,$GHz, $T = 10\,$K.

We have observed resolved superhyperfine structure (SHFS) of the B and C lines (Figures 2a and 2b, correspondingly). Two spectra differ by their appearance and characteristics. For B-center the distance between components of SHFS is equal to ∼2.3 G (11.1 MHz), the width of a component is ∼1.0 G (4.83 MHz), while for the C-center the corresponding numbers are 3.5 G (15.48 MHz) and 2.3 G (10.17 MHz).

3. Discussion

The simplest possible model of the single paramagnetic center with axial symmetry is a model with non-local ("remote") charge compensation. An admixture Yb^{3+} ion takes place in position of Cd^{2+} and forms a complex with D_{3d} symmetry consisting of the six nearest bromine ions and two cadmium ions along the C_3 axis. Other axial complexes with local charge compensation are related to the presence of small univalent ions of the Li^+ type, which takes place of Cd^{2+} neighboring with Yb^{3+} ion. Intermediate variants are possible similar to those used for the analysis of EPR spectra of Yb^{3+} ions in mixed crystals $\mathrm{Ba}_{1-x}\mathrm{La}_x\mathrm{F}_{2+x}$ [2] and Ce^{3+} ions in CaF_2 [3]. In these variants the compensation of the trivalent ion's charge is accomplished by means of alien ions and vacancies in the second, third etc. coordination spheres of paramagnetic ions. The diversity of the observed centers reflects the variety of possibilities. The rich superhyperfine structure of EPR lines ascribed to centers B and C is seen in Figures 2a and 2b. Its resolution testifies to rather high quality of the crystal and gives evidence that EPR line-width is mainly due to the nuclear spin $I = 3/2$ of bromine atom isotopes (^{79}Br, $\gamma/2\pi = 10.70$ MHz/T; ^{81}Br, $\gamma/2\pi = 11.53$ MHz/T). The remarkable difference of the number of SHFS components of two centers is noticeable. According to the famous paper by Ranon and Hyde [4], this may be due to the fact that superhyperfine interaction and Zeeman energy of ligand nuclei are of the same order of magnitude and their relative magnitude varies with the change of experimental conditions.

Acknowledgments

EPR measurements were done using the equipment of the Federal Center of Shared Facilities of Kazan Federal University and initially were supported by the state assignment in the scientific sphere allocated to Kazan University (Project no. 3.6722.2017/8.9, I.N.K.). M.R.G. and A.A.R. are thankful to Russian Science Foundation (Project no. 17-72-20053) for the opportunity to expand research.

References

1. Gafurov M.R., Iskhakova A.S., Kurkin I.N., Kurzin S.P., Malkin B.Z., Nikitin S.I., Orlinskii S.B., Rakhmatulin R.M.,Shakurov G.S., Tarasov V.F., Demirbilek R., Heber J. *SPIE Proceedings* **4166**, 279 (2002)
2. Aminov L.K., Abdulsabirov R.Y., Korableva S.L., Kurkin I.N., Kurzin S.P., Ziganshin A.G., Orlinskii S.B. *Appl. Magn. Reson.* **29**, 561 (2005)
3. Aminov L.K., Gafurov M.R., Kurkin I.N., Rodionov A.A. *Appl. Magn. Reson.* **45**, 1147 (2014)
4. Ranon U., Hyde J.S. *Phys. Rev.* **141**, 254 (1966)