

Electron Magnetic Resonance of Eu^{2+} in $\text{SrCl}_2:\text{Eu}$ Single Crystal

Soo Hyung Lee¹, Tae Ho Yeom^{1*}, and Sung-Hwan Kim²

¹Department of Laser and Optical Information Engineering, Cheongju University, Cheongju 360-764, Korea

²Department of Radiological Science, Cheongju University, Cheongju 360-764, Korea

(Received 19 August 2012, Received in final form 9 November 2012, Accepted 15 November 2012)

The electron paramagnetic resonance (EPR) of the Eu^{2+} ion in $\text{SrCl}_2:\text{Eu}$ single crystal has been investigated using an X-band spectrometer. The angular dependence of magnetic resonance positions for the Eu^{2+} impurity ion in the crystallographic *aa*-plane is analyzed with effective spin-Hamiltonian. The EPR spectra of the isolated Eu^{2+} center merged to each other. The hyperfine splitting of the isolated Eu^{2+} center due to the ^{151}Eu nucleus is approximately 35 G. Three kinds of Eu^{2+} centers except the isolated Eu^{2+} center, Eu^{2+} pairs, Eu^{2+} triples, and other Eu^{2+} clusters, are split from the fitting of the integrated experimental spectrum with the Gaussian curve. The calculated spectroscopic splitting parameters of the Eu^{2+} pairs, Eu^{2+} triples, and other Eu^{2+} clusters in $\text{SrCl}_2:\text{Eu}$ crystal are $g_1 = 2.06$, $g_2 = 1.94$, and $g_3 = 1.93$, respectively.

Keywords : EPR, $\text{SrCl}_2:\text{Eu}$ crystal, Eu^{2+} impurity, clustered Eu^{2+} ions

1. Introduction

Many kinds of inorganic scintillators have been widely used for nuclear experiments, high energy experiments, medical application, security examinations, non-destructive testing, and geological exploration [1]. However, their applications are often limited by their detection efficiency, light yield, decay time, linearity, afterglow, ruggedness or cost. There is still much interest regarding new scintillators with improved scintillation properties [2].

Eu^{2+} ions enter the strontium chloride (SrCl_2) host lattice and are studied in various areas by different methods. The photoluminescence (PL) properties of $\text{SrCl}_2:\text{Eu}$ crystals were reported [3, 4]. The scintillation properties and emission spectra of $\text{SrCl}_2:\text{Eu}$ single crystals with different Eu^{2+} concentrations were studied [2]. The ultraviolet emission spectrum and low-energy ultraviolet absorption spectra were reported for dilute $\text{SrCl}_2:\text{Eu}^{2+}$ [5]. Also, the mechanism of PL and photostimulated luminescence of $\text{SrCl}_2:\text{Eu}^{2+}$ and $\text{SrCl}_2:\text{Eu}^{2+}:\text{Na}^+$ were discussed with the formation of F centers [6]. The absorption spectra for Eu^{2+} and the relative fluorescence spectra for Eu^{2+} were measured in SrCl_2 [7]. Defects structure of pure and lightly doped SrCl_2 was studied theoretically [8].

The Eu^{2+} ion is one of the most important luminescent dopants used in scintillation materials. When the Eu^{2+} ion is added as an activator in a halide crystal, it usually substitutes for a cation in the host structure and is affected by a crystal field whose symmetry usually depends on the crystal lattice. Therefore, the EPR spectra of the Eu^{2+} ion would be interesting. EPR studies of transition metals and rare earth impurity ions in SrCl_2 single crystals had been studied [9-12]. The EPR spectra at cubic symmetry for Mn^{2+} , Gd^{3+} , and Eu^{2+} ions had been reported in SrCl_2 single crystals [9]. The cubic symmetry Eu^{2+} centre in SrCl_2 Crystal doped with Eu (0.1%) are also studied by Low [10]. The cubic-site spin-Hamiltonian parameters of Eu^{2+} in SrCl_2 have been determined by employing isotopically enriched europium (^{153}Eu , 98.8%) [11]. In SrCl_2 single crystals, however, any pairs or clustered EPR centers for Eu^{2+} ions were not reported, but only isolated Eu^{2+} EPR centers [9-12] were reported.

In this study, the EPR spectra of the Eu^{2+} impurity ion in $\text{SrCl}_2:\text{Eu}$ single crystal have been obtained and split into several spectra from the isolated Eu^{2+} and clustered Eu^{2+} impurity ions. The spectroscopic splitting parameters are calculated for the clustered Eu^{2+} centers. Four EPR centers of Eu^{2+} impurity ions, singles, pairs, triples, and other clusters, are discussed for the first time in this $\text{SrCl}_2:\text{Eu}$ crystal system.

©The Korean Magnetism Society. All rights reserved.

*Corresponding author: Tel: +82-43-229-8555

Fax: +82-43-229-8432, e-mail: thyecom@cju.ac.kr

2. Crystal Structure and Experimental Aspects

The SrCl_2 has the cubic fluorite structure with the space group of $\text{Fm}\bar{3}\text{m}$ [13]. Its lattice constant of the face-centred cube is 0.70 nm at 293 K and its melting temperature is 1146 K [13, 14]. It may be viewed as a simple cubic array of anions (chlorine ions), with alternate cube centres occupied by cations (strontium ions). The ionic arrangement can be described as a face centred cubic array of Sr^{2+} cations in which the Cl^- anions sit in all the tetrahedral interstices. A SrCl_2 was obtained in the orthorhombic form by using high pressure to convert it from its less dense established cubic symmetry and the lattice parameters of the orthorhombic form were reported [15].

A single crystal of SrCl_2 doped with Eu^{2+} ions was grown from the melt in Ar-gas atmosphere by the Czochralski method. Anhydrous SrCl_2 (Aldrich, > 99.99%) and EuCl_2 (Aldrich, 99.99%) powders were used as starting materials. Dopant material was added into the melt with a concentration of 0.5 mol%. The grown crystals were transparent.

The EPR measurements were performed using a Jeol X-band EPR spectrometer (JES-RE2X). Field modulation of 100 kHz was used to record the EPR spectra of Eu^{2+} ion in a $\text{SrCl}_2:\text{Eu}$ single crystal at room temperature. The electron magnetic resonance fields of Eu^{2+} ions in the $\text{SrCl}_2:\text{Eu}$ crystal were obtained when a magnetic field was applied from the [100] direction to the [010] direction on the crystallographic aa -plane. The typical EPR spectrum of the Eu^{2+} ion in $\text{SrCl}_2:\text{Eu}$ single crystal obtained at 9.497 GHz is shown in Fig. 1 when magnetic field B is parallel to the crystallographic $\langle 100 \rangle$ -direction. The fine

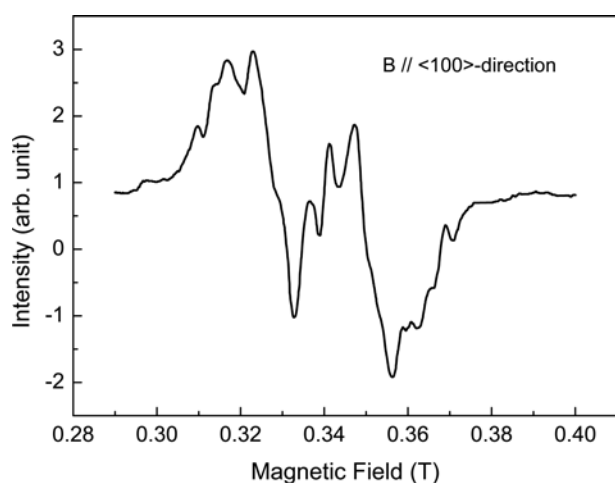


Fig. 1. Typical EPR spectra of Eu^{2+} impurity ions in the $\text{SrCl}_2:\text{Eu}$ (0.5 mol%) single crystal measured with 9.497 GHz when magnetic field B is parallel to the crystallographic $\langle 100 \rangle$ -direction.

structure and the hyperfine structure of Eu^{2+} ions by the ^{151}Eu and ^{153}Eu nuclei are not fully resolved.

3. Results and Discussion

The Eu^{2+} ion has the electron configuration $4f^7$ and is an S -state ion with $S = 7/2$ and a ground multiplet $^8S_{7/2}$. The experimental spectra of the resonance fields can be analyzed with the usual spin Hamiltonian [16, 17]. Seven sets in the fine structure of Eu^{2+} impurity ions in the $\text{SrCl}_2:\text{Eu}$ crystal are split into six lines each by the hyperfine interaction of ^{151}Eu ($I = 5/2$, 47.82% abundance) and ^{153}Eu ($I = 5/2$, 52.18% abundance) nuclei, respectively. The magnetic resonance field positions of the fine structure as well as the hyperfine structure due to the europium isotopes ^{151}Eu and ^{153}Eu nuclei for isolated Eu^{2+} impurity ions are difficult to read because the resonance lines merge together to make broad lines.

The EPR spectra having small peaks of Eu^{2+} impurity ions in Fig. 1 can be divided into four groups of spectra. The first group, small peaks on the broad lines at each angle, originates from the hyperfine structure of isolated Eu^{2+} impurity ions (singles). The number of impurities with no neighboring Eu^{2+} impurity ions within the range of interaction is denoted as singles. The spectroscopic splitting parameter and zero field splitting parameters of the isolated Eu^{2+} center could not be obtained from experimental resonance lines because all 84 resonance lines ($=7$ sets \times 12 hyperfine lines) from the fine structure with the hyperfine structure mingled with each other for each magnetic field direction.

To differentiate another three groups from the original

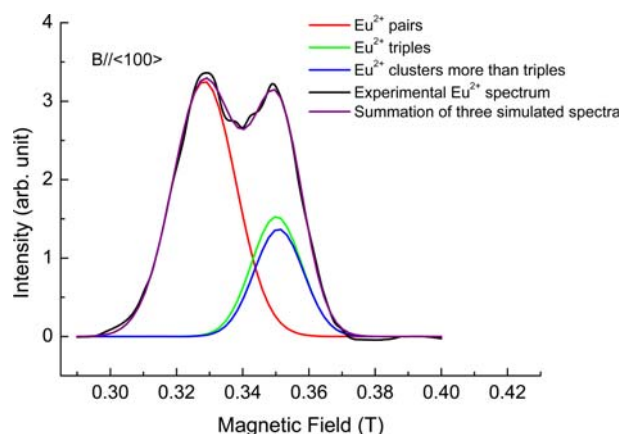


Fig. 2. (Color online) Integrated intensity of the Eu^{2+} EPR spectra in the $\text{SrCl}_2:\text{Eu}$ single crystal when magnetic field B is parallel to the crystallographic $\langle 100 \rangle$ -direction. An experimental broad line denoted by the black solid line is the sum of the three different Eu centers-pairs, triples, and the other clusters greater than triples.

spectrum, a differential EPR spectrum in Fig. 1 was integrated and simulated with three Gaussian curves. The integrated experimental spectrum of Eu^{2+} ions is denoted by the black solid line in Fig. 2. The fitted three resonance spectra with Gaussian shape curves are also shown in Fig. 2. The second group, the largest curve denoted by the red solid line, may originate from the Eu^{2+} pairs. The third group, denoted by the green solid line, may originate from Eu^{2+} triples. The fourth group, the smallest curve denoted by the blue solid line, may originate from the other Eu^{2+} clusters. The integrated experimental resonance spectra without the resolved hyperfine structure are due to the exchange interactions between Eu^{2+} ions constituting for pairs, triples, and other clusters more than triples in the $\text{SrCl}_2:\text{Eu}$ single crystal.

In the previous studies of Eu^{2+} ions in SrCl_2 single crystals [9-12], only the isolated Eu^{2+} EPR center (singles) was obtained. Whereas, at 0.5 mol% Eu concentration in our $\text{SrCl}_2:\text{Eu}$ crystal, the EPR spectra become structureless broad lines without well resolved hyperfine lines. These broad structureless lines of the Eu^{2+} impurity ions are due to the exchange interaction between the Eu^{2+} ions. In ZnS and CdS samples [18-25], however, Mn^{2+} pairs, Mn^{2+} triples, and other clustered Mn^{2+} centers were reported just like our Eu^{2+} pairs, Eu^{2+} triples, and other clustered Eu^{2+} centers in the $\text{SrCl}_2:\text{Eu}$ crystal. Ishikawa [18] explained the Mn^{2+} EPR spectra in ZnS and CdS with N divalent Mn ions coupled together by the exchange interaction between the Mn^{2+} ions theoretically and experimentally. The amounts of isolated Mn^{2+} ions, Mn^{2+} pairs, and Mn^{2+} triples in ZnS:Mn (0.35 wt%) films were estimated and simulated by observing the EPR spectra of Mn^{2+} ions [19]. The integrated EPR shape [19] of Mn^{2+} ions in ZnS:Mn for isolated Mn^{2+} ions, Mn^{2+} pairs, Mn^{2+} triples, remainder clusters, and their decomposed shapes with numerical simulations are very helpful to understand our EPR spectra of Eu^{2+} impurity ions in the $\text{SrCl}_2:\text{Eu}$ single crystal. The expected number of singles, pairs, and triples of Mn^{2+} impurity ions in a ZnS lattice were also theoretically calculated by ref [20-22]. The probabilities for singles, pairs, and different configurations of triads had been studied in a cubic and hexagonal structure [23].

The calculated spectroscopic splitting parameter g values of Eu^{2+} impurity ions for pairs, triples, and other clusters (more than triples) in the $\text{SrCl}_2:\text{Eu}$ single crystal are $g_1 = 2.06(\pm 0.06)$, $g_2 = 1.94(\pm 0.05)$, and $g_3 = 1.93(\pm 0.05)$, respectively. Our integrated broad resonance lines, constituting pairs, triples, and other clusters, of Eu^{2+} impurity ions in the $\text{SrCl}_2:\text{Eu}$ crystal may be from the higher doping of Eu concentration compared with the well resolved hyperfine resonance lines of isolated Eu^{2+} in the previous

reports [9-12]. Our EPR spectra without well resolved lines is nearly a structureless line because of the exchange interaction between Eu^{2+} ions in the $\text{SrCl}_2:\text{Eu}$ crystal. The hyperfine spectra of Eu^{2+} ion in our $\text{SrCl}_2:\text{Eu}$ crystal doped with 0.5 mol% Eu merge already into an envelope of broad resonance lines. These phenomena appear in the previous reports for Mn^{2+} impurity ions in ZnS:Mn powder [18] and Mn^{2+} in ZnS:Mn,Cu powder [24]. As the concentration of the Mn^{2+} ion increased, the Mn^{2+} spectrum changed its shape and the spectrum became a structureless single line by the exchange interaction between Mn^{2+} ions at high Mn concentration [18]. In the ZnS:Mn,Cu powder sample, the spectra of isolated Mn^{2+} ions had six hyperfine lines when the Mn^{2+} ion concentration was as low as 0.1%, whereas the six hyperfine lines gradually merged into an envelope as the Mn^{2+} ion concentration increased beyond 0.3% and the spectrum appeared as a structureless single line at a high concentration of 1.5% [24].

Hyperfine splitting of isolated Eu^{2+} impurity ion (singles) due to the ^{151}Eu nuclei in the $\text{SrCl}_2:\text{Eu}$ crystal is obtained as approximately $35(\pm 5)$ G, whereas the hyperfine splitting of the Eu^{2+} impurity ion due to ^{153}Eu could not be calculated because of the overlapping of hyperfine structure lines. This hyperfine value of Eu^{2+} due to the ^{151}Eu nucleus agrees well within the experimental accuracy with the ones previously reported [10, 12].

4. Summary

The EPR spectra of Eu^{2+} impurity ions in the $\text{SrCl}_2:\text{Eu}$ single crystal, grown by the Czochralski method, are observed in the crystallographic aa -plane at room temperature. The EPR spectra of the isolated Eu^{2+} center (singles) were mingled with each other in $\text{SrCl}_2:\text{Eu}$ doped with 0.5 mol% Eu. The calculated hyperfine splitting of the isolated Eu^{2+} impurity ion due to the ^{151}Eu nuclei in the $\text{SrCl}_2:\text{Eu}$ crystal is roughly $35(\pm 5)$ G.

The integrated experimental magnetic resonance lines except the isolated Eu^{2+} centers of Eu^{2+} impurity ions in the $\text{SrCl}_2:\text{Eu}$ (0.5 mol%) crystal are resolved into three Eu^{2+} centers, Eu^{2+} pairs, Eu^{2+} triples, and other Eu^{2+} clusters by fitting with the Gaussian shape curve. The spectroscopic splitting parameters of the three Eu^{2+} EPR centers for pairs, triples, and other clusters have been determined with effective spin Hamiltonian. The integrated experimental resonance lines without the resolved hyperfine structure are due to the exchange interactions between Eu^{2+} ions constituting pairs, triples, and other clusters greater than triples in the $\text{SrCl}_2:\text{Eu}$ single crystal.

References

- [1] G. F. Knoll, *Radiation Detection and Measurement*, Wiley, New York (1999).
- [2] J. Moon, H. Kang, H. J. Kim, W. Kim, H. Park, S. Kim, D. Kim, and S. Doh, *J. Korean Phys. Soc.* **49**, 637 (2006).
- [3] T. Kobayasi, S. Mroczkowski, and J. F. Owen, *J. Lumin.* **21**, 247 (1980).
- [4] U. Caldino, M. E. Villafuerte-Castrejon, and J. Rubio, *Cryst. Latt. Def. Amorph. Mat.* **18**, 511 (1989).
- [5] Z. Pan, L. Ning, B. M. Cheng, and P. A. Tanner, *Chem. Phys. Lett.* **428**, 78 (2006).
- [6] S. H. Kim, C. J. Kim, W. Kim, H. D. Kang, D. S. Kim, Y. K. Kim, S. H. Doh, and H. J. Seo, *Jpn. J. Appl. Phys.* **42**, 4390 (2003).
- [7] T. Kobayasi, S. Mroczkowski, J. F. Owen, and L. H. Brixner, *J. Lumin.* **21**, 247 (1980).
- [8] P. J. Bendall, C. R. A. Catlow, and B. E. F. Fender, *J. Phys. C: Solid State Phys.* **14**, 4377 (1981).
- [9] R. W. Reynolds, L. A. Boatner, and M. M. Abraham, *J. Chem. Phys.* **52**, 3851 (1970).
- [10] W. Low, *Phys. Rev.* **101**, 1827 (1956).
- [11] W. Low and U. Rosenberger, *Phys. Rev.* **116**, 621 (1959).
- [12] H. B. Utley and P. P. Mahendroo, *Chem. Phys. Lett.* **15**, 553 (1972).
- [13] M. T. Hutchings, K. Clausen, M. H. Dickens, W. Hayes, J. K. Kjems, P. G. Schnabel, and C. Smith, *J. Phys. C: Solid State Phys.* **17**, 3903 (1984).
- [14] S. Hull, S. T. Norberg, I. Ahmed, S. G. Eriksson, and C. E. Mohn, *J. Solid State Chem.* **184**, 2925 (2011).
- [15] L. H. Brixner, *Mat. Res. Bull.* **11**, 1453 (1976).
- [16] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, Oxford (1970) Chaps. 3 and 7.
- [17] S. Altschuler and B. M. Kozyrev, *Electron Paramagnetic Resonance in Compounds of Transition Elements*, Wiley, New York (1974) Chap. 3.
- [18] Y. Ishikawa, *J. Phys. Soc. Jpn.* **21**, 1473 (1966).
- [19] M. Adachi, T. Watanabe, S. Taniguchi, N. Takeuchi, S. Sakai, and H. Murakami, *J. Materials Science: Materials in Electronics* **3**, 222 (1992).
- [20] D. S. McClure, *J. Chem. Phys.* **39**, 2850 (1963).
- [21] W. H. Brumage, C. R. Yarger, and C. C. Lin, *Phys. Rev.* **133**, A765 (1964).
- [22] U. W. Pohl and H. E. Gumlich, *Phys. Rev. B* **40**, 1194 (1989).
- [23] M. M. Kreitman and D. L. Barnett, *J. Chem. Phys.* **43**, 364 (1965).
- [24] J. Li, W. Lu, and Q. Shu, *J. Lumin.* **40/41**, 836 (1988).
- [25] T. H. Yeom, Y. H. Lee, T. S. Hahn, M. H. Oh, and S. H. Choh, *J. Appl. Phys.* **79**, 1004 (1996).