

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

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The electron paramagnetic resonance (EPR) of the  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  impurity ion in the crystallographic *aa*-plane is analyzed with effective spin-Hamiltonian. The EPR spectra of the isolated  $\text{Eu}^{2+}$  center merged to each other. The hyperfine splitting of the isolated  $\text{Eu}^{2+}$  center due to the  $^{151}\text{Eu}$  nucleus is approximately 35 G. Three kinds of  $\text{Eu}^{2+}$  centers except the isolated  $\text{Eu}^{2+}$  center,  $\text{Eu}^{2+}$  pairs,  $\text{Eu}^{2+}$  triples, and other  $\text{Eu}^{2+}$  clusters, are split from the fitting of the integrated experimental spectrum with the Gaussian curve. The calculated spectroscopic splitting parameters of the  $\text{Eu}^{2+}$  pairs,  $\text{Eu}^{2+}$  triples, and other  $\text{Eu}^{2+}$  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,  $\text{Eu}^{2+}$  impurity, clustered  $\text{Eu}^{2+}$  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].

$\text{Eu}^{2+}$  ions enter the strontium chloride ( $\text{SrCl}_2$ ) 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  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  and the relative fluorescence spectra for  $\text{Eu}^{2+}$  were measured in  $\text{SrCl}_2$  [7]. Defects structure of pure and lightly doped  $\text{SrCl}_2$  was studied theoretically [8].

The  $\text{Eu}^{2+}$  ion is one of the most important luminescent dopants used in scintillation materials. When the  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  ion would be interesting. EPR studies of transition metals and rare earth impurity ions in  $\text{SrCl}_2$  single crystals had been studied [9-12]. The EPR spectra at cubic symmetry for  $\text{Mn}^{2+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Eu}^{2+}$  ions had been reported in  $\text{SrCl}_2$  single crystals [9]. The cubic symmetry  $\text{Eu}^{2+}$  centre in  $\text{SrCl}_2$  Crystal doped with Eu (0.1%) are also studied by Low [10]. The cubic-site spin-Hamiltonian parameters of  $\text{Eu}^{2+}$  in  $\text{SrCl}_2$  have been determined by employing isotropically enriched europium ( $^{153}\text{Eu}$ , 98.8%) [11]. In  $\text{SrCl}_2$  single crystals, however, any pairs or clustered EPR centers for  $\text{Eu}^{2+}$  ions were not reported, but only isolated  $\text{Eu}^{2+}$  EPR centers [9-12] were reported.

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

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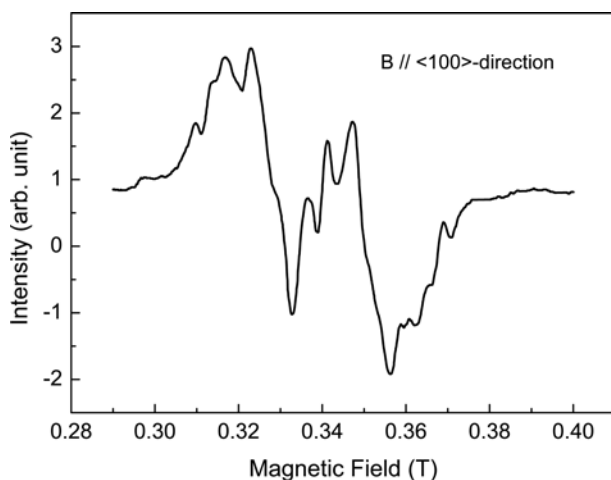
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## 2. Crystal Structure and Experimental Aspects

The  $\text{SrCl}_2$  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  $\text{Sr}^{2+}$  cations in which the  $\text{Cl}^-$  anions sit in all the tetrahedral interstices. A  $\text{SrCl}_2$  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  $\text{SrCl}_2$  doped with  $\text{Eu}^{2+}$  ions was grown from the melt in Ar-gas atmosphere by the Czochralski method. Anhydrous  $\text{SrCl}_2$  (Aldrich, > 99.99%) and  $\text{EuCl}_2$  (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  $\text{Eu}^{2+}$  ion in a  $\text{SrCl}_2:\text{Eu}$  single crystal at room temperature. The electron magnetic resonance fields of  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  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.

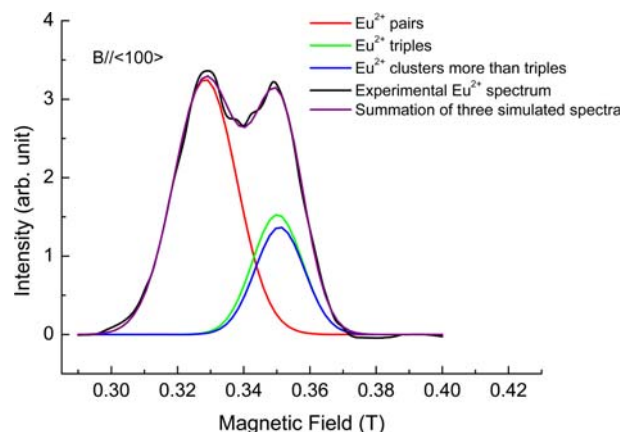
structure and the hyperfine structure of  $\text{Eu}^{2+}$  ions by the  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$  nuclei are not fully resolved.

## 3. Results and Discussion

The  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  impurity ions in the  $\text{SrCl}_2:\text{Eu}$  crystal are split into six lines each by the hyperfine interaction of  $^{151}\text{Eu}$  ( $I = 5/2$ , 47.82% abundance) and  $^{153}\text{Eu}$  ( $I = 5/2$ , 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  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$  nuclei for isolated  $\text{Eu}^{2+}$  impurity ions are difficult to read because the resonance lines merge together to make broad lines.

The EPR spectra having small peaks of  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  impurity ions (singles). The number of impurities with no neighboring  $\text{Eu}^{2+}$  impurity ions within the range of interaction is denoted as singles. The spectroscopic splitting parameter and zero field splitting parameters of the isolated  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  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  $\text{Eu}$  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  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  pairs. The third group, denoted by the green solid line, may originate from  $\text{Eu}^{2+}$  triples. The fourth group, the smallest curve denoted by the blue solid line, may originate from the other  $\text{Eu}^{2+}$  clusters. The integrated experimental resonance spectra without the resolved hyperfine structure are due to the exchange interactions between  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  ions in  $\text{SrCl}_2$  single crystals [9-12], only the isolated  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  impurity ions are due to the exchange interaction between the  $\text{Eu}^{2+}$  ions. In ZnS and CdS samples [18-25], however,  $\text{Mn}^{2+}$  pairs,  $\text{Mn}^{2+}$  triples, and other clustered  $\text{Mn}^{2+}$  centers were reported just like our  $\text{Eu}^{2+}$  pairs,  $\text{Eu}^{2+}$  triples, and other clustered  $\text{Eu}^{2+}$  centers in the  $\text{SrCl}_2:\text{Eu}$  crystal. Ishikawa [18] explained the  $\text{Mn}^{2+}$  EPR spectra in ZnS and CdS with N divalent Mn ions coupled together by the exchange interaction between the  $\text{Mn}^{2+}$  ions theoretically and experimentally. The amounts of isolated  $\text{Mn}^{2+}$  ions,  $\text{Mn}^{2+}$  pairs, and  $\text{Mn}^{2+}$  triples in ZnS:Mn (0.35 wt%) films were estimated and simulated by observing the EPR spectra of  $\text{Mn}^{2+}$  ions [19]. The integrated EPR shape [19] of  $\text{Mn}^{2+}$  ions in ZnS:Mn for isolated  $\text{Mn}^{2+}$  ions,  $\text{Mn}^{2+}$  pairs,  $\text{Mn}^{2+}$  triples, remainder clusters, and their decomposed shapes with numerical simulations are very helpful to understand our EPR spectra of  $\text{Eu}^{2+}$  impurity ions in the  $\text{SrCl}_2:\text{Eu}$  single crystal. The expected number of singles, pairs, and triples of  $\text{Mn}^{2+}$  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  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  in the previous

reports [9-12]. Our EPR spectra without well resolved lines is nearly a structureless line because of the exchange interaction between  $\text{Eu}^{2+}$  ions in the  $\text{SrCl}_2:\text{Eu}$  crystal. The hyperfine spectra of  $\text{Eu}^{2+}$  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  $\text{Mn}^{2+}$  impurity ions in ZnS:Mn powder [18] and  $\text{Mn}^{2+}$  in ZnS:Mn,Cu powder [24]. As the concentration of the  $\text{Mn}^{2+}$  ion increased, the  $\text{Mn}^{2+}$  spectrum changed its shape and the spectrum became a structureless single line by the exchange interaction between  $\text{Mn}^{2+}$  ions at high Mn concentration [18]. In the ZnS:Mn,Cu powder sample, the spectra of isolated  $\text{Mn}^{2+}$  ions had six hyperfine lines when the  $\text{Mn}^{2+}$  ion concentration was as low as 0.1%, whereas the six hyperfine lines gradually merged into an envelope as the  $\text{Mn}^{2+}$  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  $\text{Eu}^{2+}$  impurity ion (singles) due to the  $^{151}\text{Eu}$  nuclei in the  $\text{SrCl}_2:\text{Eu}$  crystal is obtained as approximately  $35(\pm 5)$  G, whereas the hyperfine splitting of the  $\text{Eu}^{2+}$  impurity ion due to  $^{153}\text{Eu}$  could not be calculated because of the overlapping of hyperfine structure lines. This hyperfine value of  $\text{Eu}^{2+}$  due to the  $^{151}\text{Eu}$  nucleus agrees well within the experimental accuracy with the ones previously reported [10, 12].

#### 4. Summary

The EPR spectra of  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  impurity ion due to the  $^{151}\text{Eu}$  nuclei in the  $\text{SrCl}_2:\text{Eu}$  crystal is roughly  $35(\pm 5)$  G.

The integrated experimental magnetic resonance lines except the isolated  $\text{Eu}^{2+}$  centers of  $\text{Eu}^{2+}$  impurity ions in the  $\text{SrCl}_2:\text{Eu}$  (0.5 mol%) crystal are resolved into three  $\text{Eu}^{2+}$  centers,  $\text{Eu}^{2+}$  pairs,  $\text{Eu}^{2+}$  triples, and other  $\text{Eu}^{2+}$  clusters by fitting with the Gaussian shape curve. The spectroscopic splitting parameters of the three  $\text{Eu}^{2+}$  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  $\text{Eu}^{2+}$  ions constituting pairs, triples, and other clusters greater than triples in the  $\text{SrCl}_2:\text{Eu}$  single crystal.

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