Inhomogeneous broadening of ESR lines of rare earth impurities in scheelite CaWO$_4$ induced by internal electric field gradients

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Abstract. The inhomogeneous broadening of ESR line in erbium-doped CaWO$_4$ crystal is studied both theoretically and experimentally in the special case when external magnetic field is parallel to crystal $c$ axis. Lorenzian shapes of ESR lines are observed and ascribed to the broadening from random electric field gradients produced by charged defects. The defect concentrations are estimated on the grounds of a simple statistical model and crystal-field calculations of impurity-defect coupling constants. Samples with different concentrations of erbium ions are used in order to find out how Er$^{3+}$ impurities affect the linewidth.

1. Introduction
As is well-known, crystal lattice imperfections lead to the inhomogeneous broadening of ESR lines in crystals since the perturbation of the crystal field randomly shifts Larmor frequencies of paramagnetic ions. This occurs because energy levels and effective $g$-factors of paramagnetic impurities (especially in case of rare earth ions) are extremely sensitive to variations of positions and charges of the neighboring ions. The possible lattice defects are various: point charges and consequent local strains, dislocations, mosaic structure [1]. Not taking into account random defects that are always introduced into the crystal during the process of its growth, the broadening is unavoidable in case when initially diamagnetic host matrix is activated with paramagnetic ions. Among the above-mentioned, the role of charged defects is appreciable since they produce electric field $E \sim 1/R^2$ slowly diminishing with distance $R$ between the paramagnetic ion and the defect. These charged defects appear most naturally in case of heterovalent substitution, as in rare earth-doped scheelite crystals. In case when ESR line broadening is solely due to paramagnetic impurity, Larmor frequencies $\omega_1, \omega_2$ and the distance between the two given paramagnetic ions become correlated. Note that most statistical models of magnetic relaxation in magnetically diluted media do not take into account the above-mentioned correlations. These correlations become important when the corresponding transition probabilities depend on $|\omega_1 - \omega_2|$, as in the case of relaxation induced by interspin dipolar interactions [2, 3]. To summarize, in every theoretical study of magnetic relaxation that involves interspin interactions one must determine leading line broadening mechanisms that take place in the system.

These mechanisms can be revealed either in experimental or theoretical studies of the system. The former involve observations of shapes and widths of resonance lines; when magnetic anisotropy is

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present, one can also vary the direction of static magnetic field vector $H_0$. The latter are direct
calculations of the lineshapes based on the knowledge of relevant broadening mechanisms, impurity-
defect coupling constants and defect concentration. In most cases this task is highly time-consuming,
and only crude estimations are possible. In case of dislocations, the calculated linewidths are very
approximate [1]. As for charged point defects, general model based on continuum approximation
 predicts Holtsmark and Lorenzian lineshapes in the presence of random electric fields and electric
field gradients, respectively [1].

In the present paper we study both theoretically and experimentally the inhomogeneous broadening
of ESR line in erbium-doped CaWO$_4$ crystal in the special case when external magnetic field is
parallel to crystal $c$ axis. We observe Lorenzian shapes of ESR lines and ascribe the broadening to
random electric field gradients produced by charged defects. Based on a statistical model [1] and on
our crystal-field calculations of impurity-defect coupling constants, we estimate the defect
concentrations. A similar problem was studied before for Er$^{3+}$ in MgO crystal [4]. Our study
essentially differs from ref. [4] since we use samples with different concentrations of erbium ions in
order to find out how Er$^{3+}$ impurities affect the linewidth. The answer to this question is crucial since
rare-earth-activated scheelites are frequently used in magnetic resonance experiments and were
proposed as promising solid state media for the implementation of quantum computation [5, 6].

2. Theoretical background
We will briefly outline the procedure that enables to account for the random shifts of Larmor
frequencies of rare earth (RE) ions due to their electrostatic interactions with charged point defects.
We start with the electrostatic potential at the site of an electron of RE ion produced by the defect:

$$\varphi(R, r) = -\frac{qe}{|R - r|} = qe \sum_{p=0}^{\infty} \sum_{k=-p}^{p} R^p R^p C^p_k \Theta(\Theta, \Phi) C^p_k (\vartheta, \varphi),$$

(1)

where vectors $R(r, \vartheta, \varphi)$ and $C^p_k (\Theta, \Phi)$ determine positions of the defect and the electron in
spherical coordinates with respect to the nucleus of RE ion, $q$ is the excessive charge of the defect in
units of elementary charge $e$, and $C^p_k$ are spherical operators. Since $r \parallel R$, one can leave only the
first few terms of the multipolar expansion (1). The constant term with $p=0$ can be omitted. We will
take only dipolar and quadrupolar terms $p=1$ and $p=2$ that correspond to electric field and electric
field gradient of the defect, respectively.

If there are $n$ electrons on the valency 4$f$ shell of RE ion and $N$ defects in the crystal, the
perturbation of the crystal field at the site of RE ion will be as follows:

$$\delta\mathcal{H}_{CF} = -e \sum_{j=1}^{n} \sum_{j=1}^{N} \varphi(R_j, r).$$

(2)

The perturbation $\delta\mathcal{H}_{CF}$ alters eigenstates and energy splittings in Zeeman structure of the specter
of RE ion. Since $p=1$ terms do not mix the states inside 4$f$ shell, they are involved only in
transitions via upper-lying configuration. Thus, despite the fact that $p=2$ terms are lesser in
magnitude than $p=1$ terms, their final contributions into the frequency shift can be significant.
Generally, it is hard to distinguish between dipolar and quadrupolar contributions from the
experimentally observed lineshapes.

In CaWO$_4$ scheelite, trivalent RE ions occupy positions of Ca$^{2+}$ with $S_4$ point symmetry. The ESR
line broadening in that particular crystal due to random electric fields from charged point defects when
the vector $H_0$ is perpendicular to the crystal $c$ axis was thoroughly investigated in ref. [7]. However,
when $H_0 \parallel c$, the terms with $p=1$ do not shift Larmor frequencies in the lowest order of perturbation
theory due to symmetry selection rules [7, 8] and can be neglected. So we have here a special case
when we are able to investigate solely $p=2$ contributions. Moreover, it is straightforward to show on
the same symmetry grounds that only $C_{20}(\mathcal{O}, \mathcal{Q}_j\mathcal{Q}_k)$ operators would alter the energy splittings, and the perturbation (2) takes the form

$$\delta H_{\text{CF}} = -\mathcal{e}^2 \sum_{j=1}^{N} \sum_{j=1}^{N} \frac{q_j r_j^2}{R_j^3} C_{20}(\mathcal{O}_j, \Phi_j) C_{20}(\mathcal{O}_k, \Phi_k).$$

(3)

Since for rare earths the total angular moment $J$ is a good quantum number, it is possible to project the operator (3) onto a basis $|JM\rangle$ of $J_z$ eigenstates of the lowest multiplet $25+1L_j$:

$$\langle JM | \delta H_{\text{CF}} | JM' \rangle = -\alpha_j \mathcal{e}^2 \langle r^2 \rangle \sum_{j=1}^{N} \frac{q_j C_{20}(\mathcal{O}_j, \Phi_j)}{R_j^3},$$

(4)

were the coefficient $\alpha_j$ is the reduced matrix element [9] and $\langle r^2 \rangle$ is the average value of $r^2$ of an electron in $4f$ shell. We will omit the brackets $|JM\rangle$ henceforth. Recalling that $C_{20} = O_{20}/2$ where $O_{20}$ is Stevens operator, and that $C_{20}(\mathcal{O}_j, \Phi_j) = (3 \cos^2 \Theta_j - 1)/2$, we rewrite (4) as

$$\delta H_{\text{CF}} = \frac{\alpha_j \mathcal{e}^2 (1 - \sigma_j)}{4} \sum_{j=1}^{N} \frac{q_j (1 - 3 \cos^2 \Theta_j)}{R_j^3} O_{20} \equiv \alpha_j \delta B_{20} \cdot O_{20},$$

(5)

where the factor $(1 - \sigma_j)$ is added to account for the shielding from 5s, 5p and 6s outer shells. The effective Hamiltonian of RE ion is now

$$H = \sum_{j \neq k} \alpha_{jk} B_{jk} O_{jk} + g_{J Z} \mu_B H_0 J_z + \alpha_J \delta B_{20} \cdot O_{20},$$

(6)

where the first two terms represent interactions with crystal field and external magnetic field. Suppose that $n$ is an odd number, and the energy levels of RE ion when $H_0 = 0$ are at least twice degenerate. The degeneracy is removed when $H_0 \neq 0$. Then it is possible to introduce an effective spin $s = 1/2$ and $g$ -factor $g_{J Z}$ for a given Kramers doublet. The last term in (6) shifts Larmor angular frequency $\omega$ by the value $\delta \omega$ so that

$$\delta \omega = \frac{\delta E_z - \delta E_n}{h} = \frac{1}{g_{J Z}} \frac{2}{1 + 1/2} \sum_{j=1}^{N} \frac{\langle 2 | O_{20} | m \rangle \langle m | J_z | 2 \rangle + c.c.}{E_z - E_n} \equiv G \omega \sum_{j=1}^{N} \frac{q_j (1 - 3 \cos^2 \Theta_j)}{R_j^3},$$

(7)

where $E_1, E_2, \ldots, E_{2J+1}$ are energy levels of the multiplet when $H_0 = 0$, $\delta E_n$ are their shifts due to electric field gradients in the presence of $H_0$, $\delta E_z = -\delta E_z$, and indices 1, 2 are those of the given Kramers doublt $(E_2 > E_1$ for nonzero $H_0$). The expression (7) is similar to the one obtained for the shift $\delta \omega_d$ due to dipolar interactions,

$$\delta \omega_d = \omega_d = \frac{g_{J Z} \mu_B^2}{8h} \sum_{j} \frac{m_j (1 - 3 \cos^2 \Theta_j)}{R_j^3},$$

where

$$m_j/2 = \pm 1/2$$

accounts for the random orientation of $j$-th spin with respect to z axis. Under continuum approximation of statistical theory after the integration over all possible $R_j$ the expression (8) results in Lorenzian lineshape with half-width $\Delta \omega_d = 4 \pi^2 \left(9 \sqrt{3} h \right)^{-1} C g_{J Z} \mu_B^2$ [2], where $C$ is the concentration of RE ions. The substitution Ca$^{2+} \rightarrow$RE$^{3+}$ in scheelite with excessive charge $q_+ = 1$ demands additional charge compensators with $q_- < 0$. In common case of Na$^+$ compensation $q_- = -1$, and the analogy with (8) is complete if we formally replace $q_j$ with $m_j$. The resulting lineshape in case of random electric field gradients produced by defects of unit charge $\pm q$ and concentration $C_q$ is Lorenzian with linewidth
\[ \sigma = \frac{8\pi^2}{9\sqrt{3}} C_q |qG| \omega . \]  

When there are several defect species with different $|q|$, one has to sum up the contributions (9) from all species to obtain the total half-width of ESR line. In the simplest case when the only charged defects in the crystal are RE$^{3+}$ and Na$^+$ ions, one has $|q|=1$ and $C_q = 2C_{RE}$.

3. Results and discussion

ESR spectra of two samples of CaWO$_4$:Er$^{3+}$ crystals grown with natrium compensation and nominal erbium concentrations 0.05 at. % and 0.2 at. % (samples no. 1 and 2 henceforth) were acquired using Bruker ESP 300 X-band spectrometer at the frequency 9.4 GHz, temperature 10 K and $B_0 \parallel c$. The ESR lines of different erbium isotopes proved to be Lorentzian, as expected in case of the broadening due to random electric field gradients. A part of ESR spectrum of the sample no. 2 corresponding to central line (zero nuclear spin) is presented in figure 1. The inhomogeneous half-widths $\sigma$ of the central lines for both samples are presented in table 1.

![ESR spectrum](image)

**Figure 1.** The central line (corresponding to erbium isotopes with zero nuclear spins) of ESR spectrum of the sample no. 2. Experimental data, fits to Lorenzian and Gaussian distributions are represented by black solid, blue dashed and red dotted lines, respectively.

The crystal field parameters $B_{pk}$, as well as the parameters $\alpha_2 = 0.620$, $\langle r^2 \rangle = 0.353$ Å, $g_f = 6/5$ and $\alpha_2 = 4/1575$ for the lowest multiplet $^4I_{15/2}$ of the ground configuration $4f^{11}$ of Er$^{3+}$ ions were taken from literature data. The coupling coefficient $G = -3.2 \cdot 10^{-23}$ cm$^3$ in Eq. (9) was established for its lowest Kramers doublet with $g_z = 1.25$ via direct diagonalization of the Hamiltonian (6). The
defect concentrations $C_q$ assuming $q = \pm 1$ were obtained from the fit to experimental $\sigma$ values by means of Eq. (9).

In order to determine the role of Er$^{3+}$ charged defects in the broadening of ESR lines we needed to know real Er$^{3+}$ concentrations $C_{\text{RE}}$ in the samples. They were obtained by means of comparison of erbium ESR spectra with those of standard samples with known impurity concentrations acquired under the same experimental conditions. Real concentrations turned out to be somewhat smaller: 0.021 at. % and 0.036 at. % for the samples no. 1 and 2, respectively. The relative error of concentration measurements was 30 %. Thus the values $2C_{\text{RE}}$ were less than $C_q$ by nearly a factor of 4. Dipolar broadening was found negligible (the last column of table 1).

Table 1. Inhomogeneous half-widths, charged defect concentrations, erbium-induced excessive charge concentrations and dipolar half-widths obtained for the central ESR lines of the samples no. 1 and 2.

| Sample no. | $\sigma / 2\pi$, MHz | $C_q$, $10^{19}$ cm$^{-3}$ | $2C_{\text{RE}}$, $10^{19}$ cm$^{-3}$ | $\Delta\omega_d / 2\pi$, MHz |
|------------|---------------------|--------------------------|-------------------------------|--------------------------|
| 1          | 35                  | 2.3                      | 0.52±0.16                     | 0.07±0.02                |
| 2          | 56                  | 3.7                      | 0.91±0.27                     | 0.12±0.04                |

4. Conclusions
Careful studies of ESR lines in CaWO$_4$:Er$^{3+}$ crystal samples show that primary contributions to the observed linewidths do not come from impurity erbium ions. While there may be other charged defects with considerable concentrations, another possible broadening mechanisms like random strains and dislocation dipoles are known to produce the same Lorentzian lineshapes [1].

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