

Determination of the internal stress distribution parameters alpha and beta for Fe³⁺-doped yttrium aluminium garnet crystals from the electron paramagnetic resonance linewidth and spin-lattice coupling coefficients

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 177

(<http://iopscience.iop.org/0953-8984/3/2/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:03

Please note that [terms and conditions apply](#).

Determination of the internal stress distribution parameters α and β for Fe^{3+} -doped yttrium aluminium garnet crystals from the electron paramagnetic resonance linewidth and spin–lattice coupling coefficients

Zheng Wen-Chen

Department of Material Science, Sichuan University, Chengdu 610064, People's Republic of China and International Center for Materials Physics, Academia Sinica, Shenyang 110015, People's Republic of China

Received 19 June 1990

Abstract. In this paper the spin–lattice coupling coefficients G_{11} and G_{44} for Fe^{3+} ions in both octahedral and tetrahedral sites of YAG crystals have been calculated within the framework of the cubic field approximation from our simple and uniform method of calculating these coefficients in two cubic (O_h and T_d) symmetries by using the parameters obtained from the optical spectra. The results can satisfactorily explain the uniaxial-stress EPR experiments for the two sites and are reasonable. On this basis, the parameters α and β that characterize the distributions of internal stresses and strains are determined for the two sites from the distinctive linewidth data of EPR spectra. It appears that our above method can be used to study the internal stress distributions for the crystals containing paramagnetic ions, particularly in the absence of experimental data of spin-lattice coupling coefficients.

As is well known, when a crystal contains a high concentration of defects or is poorly annealed, a random distribution of the internal stresses and strains is caused in the crystal. In general, the various internal stress components at a site can be assumed to be uncorrelated and hence the distribution of stress components is Gaussian type [1–3]. Thus, for cubic crystals, the distributions are given by [1]

$$P(X_{11}) = P(X_{22}) = P(X_{33}) = (2/\pi)^{1/2} \alpha^{-1} \exp(-2X_{ii}^2/\alpha^2) \quad (1)$$

$$P(X_{12}) = P(X_{23}) = P(X_{13}) = (2/\pi)^{1/2} \beta^{-1} \exp(-2X_{ij}^2/\beta^2) \quad (2)$$

where X_{ij} are the stress components along the cubic axes. α and β are the parameters that characterize the distribution of internal stresses in a crystal. As a result of these internal stresses in the crystals containing paramagnetic ion impurities, anisotropic broadening of linewidth in EPR spectra can be observed [1–3]. So, from these linewidth data, some useful information about the distributions of internal stresses and strains in the vicinity of impurity ions can be obtained. However, the internal stress distribution parameters α and β cannot be directly measured experimentally. From the linewidth data of EPR spectra, one can obtain only the absolute values of parameters $C_{11}\alpha$ and $C_{44}\beta$

for paramagnetic ions in a cubic crystal [1]. The parameters C_{11} and C_{44} (using the contracted Voigt notation) are the spin-lattice coupling coefficients defined by [1]

$$D_{ij} = \sum_{k,l} C_{ijkl} X_{kl} \quad (3)$$

where D_{ij} are the strain-induced shift of zero-field splitting.

Because the coefficients C_{11} and C_{44} may be considerably different from crystal to crystal and ion to ion, to understand better the character of the internal stress distribution, it is necessary to separate the parameters α and β from $C_{11}\alpha$ and $C_{44}\beta$. So, the theoretical calculations of coefficients C_{11} and C_{44} are of significance, particularly in the absence of the experimentally determined values of C_{11} and C_{44} . As is known, both the tensor \mathbf{C} and the tensor \mathbf{G} can be used to stand for the spin-lattice coupling coefficients. They are related by the elastic compliance constants s_{ij} [4], i.e.

$$C_{ijkl} = G_{ijrs} s_{rskl}. \quad (4)$$

Thus, for cubic symmetry in which there are only two independent coefficients, we have

$$C_{11} = G_{11}(s_{11} - s_{12}) \quad C_{44} = G_{44}s_{44}. \quad (5)$$

So, one can obtain the coefficients C_{11} and C_{44} by calculating the coefficients G_{11} and G_{44} . In our previous papers [5-9], for the calculations of coefficients G_{11} and G_{44} for d^n ions in two cubic (O_h and T_d) symmetries, a simple and uniform method has been developed and gave reasonable results for many crystals on comparison with experimental findings. It appears that the method can also be used to study the internal stress distribution parameters α and β . In this paper, we shall use it to calculate the coefficients G_{11} and G_{44} for Fe^{3+} ions in both octahedrally and tetrahedrally coordinated sites of yttrium aluminium garnet (YAG) crystals within the framework of the cubic field approximation. On this basis, the parameters α and β are determined from the EPR linewidth data for the two sites.

Garnets have a cubic structure (space group, $Ia3d$). The structure with its three distinct cationic sites having different local symmetries is a potentially interesting system for examining the various theories. Fe^{3+} ions enter substitutionally for Al^{3+} ions in the YAG crystal and occupy the octahedral (or sixfold oxygen-coordinated) site (called the a site) and the tetrahedral site (the d site) [2]. The local symmetries for both sites are axial. The a site has a small trigonal (C_{3v}) distortion along the local z axis which is coincident with the crystal [111] axis, whereas the d site has a small tetragonal (S_4) distortion along the crystal [100] direction. The parameters $C_{11}\alpha$ and $C_{44}\beta$ for the two sites were measured with the approximation of cubic symmetry from the anisotropic line broadening of EPR spectra [2], but the coefficients C_{11} and C_{44} are not reported. So, the parameters α and β are not determined. In the following, we first calculate the coefficients G_{11} and G_{44} for the two sites.

For d^n ions in sixfold cubic (O_h) coordination, this simple and uniform method is [5-7]†

$$G_{11} = -\frac{1}{3}(\partial D_{\text{tetra}}/\partial \alpha')_0 \quad G_{44} = -(\sqrt{2}/6)(\partial D_{\text{tet}}/\partial \beta')_0. \quad (6)$$

From (6) and the high-order perturbation formulae of zero-field splitting for d^5 ions in tetragonal and trigonal symmetries based on the spin-orbit coupling mechanism which

† To avoid confusion with the internal stress distribution parameters, the angles α and β in [5-9] are written as α' and β' in this paper.

is believed to be of importance to zero-field splitting [10], we yield the analytic expressions of coefficients G_{11} and G_{44} for d⁵ ions in O_h symmetry [7]:

$$G_{11} = \frac{40q\xi^2 D_q^2}{P^2 G} - \frac{18\xi^3 eq(1 + 3p/eR_0)\langle r^2 \rangle}{P^2 DR_0^3} \quad (7)$$

$$G_{44} = -20\xi^2 D_q^2/P^2 G + \frac{8\xi^3 eq(1 + 3p/eR_0)\langle r^2 \rangle}{P^2 DR_0^3} \quad (8)$$

with

$$P = 7B + 7C + 2\alpha'' \quad D = 17B + 5C + 6\alpha'' \quad G = 10B + 5C + 20\alpha'' \quad (9)$$

(where α'' is the Trees correction) and

$$D_q = -eq(1 + 5p/eR_0)\langle r^4 \rangle/6R_0^5 \quad (10)$$

where q is the ligand charge and p the dipole.

On the other hand, for dⁿ ions in fourfold cubic (T_d) coordination, we have [8, 9]

$$G_{11} = -(2\sqrt{2}/9)(\partial D_{\text{tetra}}/\partial \alpha')_0 \quad (11)$$

$$G_{44} = \frac{8}{3}(\partial D_{\text{tet}}/\partial \ln R_1)_0 - (\sqrt{2}/9)(\partial D_{\text{tet}}/\partial \beta')_0.$$

Similarly, from the same high-order perturbation formulae of zero-field splitting in tetragonal and trigonal symmetries, we obtain [8]

$$G_{11} = -\frac{320}{3}\xi^2 D_q^2/P^2 G + \frac{8\xi^3 eq(1 + 3p/eR_0)\langle r^2 \rangle}{P^2 DR_0^3} \quad (12)$$

$$G_{44} = 100\xi^2 D_q^2/P^2 G - \frac{8\xi^3 eq(1 + 3p/eR_0)\langle r^2 \rangle}{P^2 DR_0^3} \quad (13)$$

with

$$D_q = \frac{2}{7}eq(1 + 5p/eR_0)\langle r^4 \rangle/R_0^5. \quad (14)$$

Obviously, equations (7) and (8) are applicable for Fe³⁺ in the a site, and equations (12) and (13) for the d site. Interestingly, the signs of G_{11} and G_{44} are opposite for the two cubic cases.

From the empirical d orbital of Fe³⁺ ions obtained from the optical spectra data of many crystals containing Fe³⁺ ions [11], we have

$$\begin{aligned} B_0 &= 1130.22 \text{ cm}^{-1} & C_0 &= 4111.45 \text{ cm}^{-1} & \xi_0 &= 588.946 \text{ cm}^{-1} \\ \langle r^2 \rangle_0 &= 1.89039 \text{ au} & \langle r^4 \rangle_0 &= 11.46485 \text{ au}. \end{aligned} \quad (15)$$

Introducing a parameter N to denote the average reduction due to the covalency effect, one gets

$$B = N^4 B_0 \quad C = N^4 C_0 \quad \xi = N^2 \xi_0 \quad \langle r^k \rangle = N^2 \langle r^k \rangle_0. \quad (16)$$

The parameters N and p and the Trees correction α'' can be determined from the optical spectra for the two sites. For the a site, the values of $N = 0.894$, $p = 0.045eR_0$ and $\alpha'' = 10 \text{ cm}^{-1}$ are found to give a good fit to the observed optical spectra [12], and for the d site the good fit values are $N = 0.906$, $p = 0.014eR_0$ and $\alpha'' = 80 \text{ cm}^{-1}$.

Table 1. Experimental and calculated positions of optical spectra bands for YAG:Fe³⁺ crystals.

Experiment [12] Wavenumber (cm ⁻¹)	Calculation			
	a site		d site	
	Wavenumber (cm ⁻¹)	Transition	Wavenumber (cm ⁻¹)	Transition
10 400	10 031	⁴ T ₁ (⁴ G)		
14 300	14 734	⁴ T ₂ (⁴ G)		
16 000			16 360	⁴ T ₁ (⁴ G)
19 400			20 535	⁴ T ₂ (⁴ G)
20 460 } 20 510 } 21 180 }	20 790	{ ⁴ A ₁ , ⁴ E(⁴ G)		
22 880	23 138	⁴ T ₂ (⁴ D)		
24 030			23 022	⁴ A ₁ , ⁴ E(⁴ G)
24 440	25 513	⁴ E(⁴ D)		
25 200 } 25 540 } 25 870 }			25 575	⁴ T ₂ (⁴ D)
26 300 } 26 670 }			27 162	⁴ E(⁴ D)

Comparison between the calculated and experimental optical spectra is shown in table 1. Thus, substituting the distinctive parameters N , p and α'' and the structural datum R_0 (the cation–ligand distance for the a site of the YAG crystal is $R_0 = 1.937 \text{ \AA}$ and for the d site is $R_0 = 1.761 \text{ \AA}$ [13]) into the above formulae related to different sites, we get for the a site

$$G_{11}(a) = 4.47 \text{ cm}^{-1} \quad G_{44}(a) = -0.81 \text{ cm}^{-1} \quad (17)$$

and for the d site

$$G_{11}(d) = -1.33 \text{ cm}^{-1} \quad G_{44}(d) = 1.16 \text{ cm}^{-1}. \quad (18)$$

It is noteworthy that some of the calculated results can be supported by the uniaxial-stress EPR experiments on YAG:Fe³⁺ crystals. Hodges [14] measured the changes in the zero-field splitting for Fe³⁺ ions in the two sites of YAG crystals induced by stress (along the local symmetry axis) and obtained for the a site

$$dD/dP_{\parallel c_3} = 6.27 \times 10^{-13} \text{ cm dyn}^{-1} \quad (19)$$

and for the d site

$$dD/dP_{\parallel c_4} = 8.13 \times 10^{-13} \text{ cm dyn}^{-1}. \quad (20)$$

For the a site, from the phenomenal and macroscopic thermodynamic analysis, we have

$$dD/dP = [\partial D/\partial(\ln R)][\partial(\ln R)/\partial P] + (\partial D/\partial\beta')(\partial\beta'/\partial P) \quad (21)$$

where R denotes the bonding length.

Table 2. The internal stress distribution parameters α and β for paramagnetic ions in some crystals.

	α (kg cm ⁻²)	β (kg cm ⁻²)
MgO:Fe ³⁺ [1]	112	80
MgO:Mn ²⁺ [1]	104	96
MgO:Cr ³⁺ [17]		75
YAG:Fe ³⁺ (a site)	22.6	137
YAG:Fe ³⁺ (d site)	92.5	289

For simplicity, we apply the cubic symmetry approximation; then

$$\partial D/\partial(\ln R) = 0. \quad (22)$$

So, one gets [5, 7]

$$dD/dP \approx (\partial D/\partial\beta')(\partial\beta'/\partial P) = -G_{44}s_{44}. \quad (23)$$

The elastic constants of YAG crystals are [15]

$$s_{11} = 3.62 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1} \quad s_{12} = -0.887 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1} \quad (24)$$

$$s_{44} = 8.8 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}.$$

Then

$$G_{44}(a) \approx -0.71 \text{ cm}^{-1}. \quad (25)$$

The result is in agreement with our calculated value. More exactly, we can take into account the contribution of $\partial D/\partial(\ln R)$ due to trigonal distortion. From the following reasonable estimate, we can find that the agreement is even better. By assuming that $D \sim R^n$, we have

$$\partial D/\partial(\ln R) = nD. \quad (26)$$

From the zero-field splitting D ($\approx -0.105 \text{ cm}^{-1}$ [14]) of the a site and the value of n (≈ -10 for d⁵ ions in various low symmetries [16]), we have

$$\partial D/\partial(\ln R) \approx 1.05 \text{ cm}^{-1}. \quad (27)$$

From [1],

$$\partial(\ln R)/\partial P \approx -\frac{1}{3}(s_{11} + 2s_{12}) = -0.615 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}. \quad (28)$$

Substituting (27) and (28) into (21), we obtain

$$G_{44}(a) \approx -0.78 \text{ cm}^{-1}. \quad (29)$$

The result is close to our calculated value.

Similarly, for the d site,

$$dD/dP = [\partial D/\partial(\ln R)][\partial(\ln R)/\partial P] + (\partial D/\partial\alpha')(\partial\alpha'/\partial P). \quad (30)$$

Within the cubic symmetry approximation [5],

$$dD/dP \approx (\partial D/\partial\alpha')(\partial\alpha'/\partial P) = -\frac{2}{3}G_{11}(s_{11} - s_{12}). \quad (31)$$

Then

$$G_{11}(d) = -1.20 \text{ cm}^{-1}. \quad (32)$$

The result is also similar to our calculated value. In an analogous manner, the more

exact result obtained by taking into account the contribution of $\partial D/\partial(\ln R)$ due to tetragonal distortion is $G_{11}(d) = -1.29 \text{ cm}^{-1}$ (note that, for the d site, $D = -0.0987 \text{ cm}^{-1}$ [14], $\partial(\ln R)/\partial P \approx -\frac{1}{3}(s_{11} + s_{12}) = -0.615 \times 10^{-13} \text{ cm}^2 \text{ dyn}^{-1}$). The value is more consistent with the calculated value. In short, our calculated results can explain satisfactorily the stress dependences of EPR spectra for the two sites and can be regarded as reasonable. In addition, this shows that the cubic symmetry approximation for Fe^{3+} in both sites of YAG crystals is suitable.

Obviously, from (5), (17), (18) and (24), the coefficients C_{11} and C_{44} can be obtained easily for the two sites of Fe^{3+} ions in YAG crystals. Thus, according to the parameters $C_{11}\alpha$ and $C_{44}\beta$ for YAG: Fe^{3+} crystals (for the a site, $|C_{11}\alpha| = 0.467 \times 10^{-4} \text{ cm}^{-1}$ and $|C_{44}\beta| = 1 \times 10^{-4} \text{ cm}^{-1}$; for the d site, $|C_{11}\alpha| = 0.567 \times 10^{-4} \text{ cm}^{-1}$ and $|C_{44}\beta| = 3 \times 10^{-4} \text{ cm}^{-1}$ [2]), we can obtain the internal stress distribution parameters α and β for both sites. The results, as well as those obtained from experimental values of C_{11} and C_{44} for Fe^{3+} , Mn^{2+} and Cr^{3+} in MgO crystals [1, 17] are shown in table 2. It can be seen that the parameters α and β in the two sites of YAG: Fe^{3+} crystals can be compared with those of Fe^{3+} , Mn^{2+} and Cr^{3+} in MgO crystals. In addition, the parameters α and β are larger for Fe^{3+} in the tetrahedral d site. These results are qualitatively reasonable in view of the smaller size of the tetrahedral site compared with the octahedral site. So, our results on α and β should be reasonable.

Acknowledgment

This project was supported by the National Natural Science Foundation of China.

References

- [1] Feher E R 1964 *Phys. Rev.* **136** A145
- [2] Serway R A, Yang F-H and Marshall S A 1978 *Phys. Status Solidi* **b 89** 267
- [3] Bai X-M and Zeng L-W 1989 *Phys. Rev.* **B 39** 10
- [4] Blanchard C, Parrot R and Boulanger D 1973 *Phys. Rev.* **B 7** 4072
- [5] Zheng W-C 1989 *Phys. Rev.* **B 40** 7292
- [6] Zheng W-C 1989 *J. Phys.: Condens. Matter* **1** 8093
- [7] Zheng W-C 1989 *J. Phys.: Condens. Matter* **1** 5667
- [8] Zheng W-C 1990 *Phys. Rev.* **B 42** 826
- [9] Zheng W-C 1990 *Phys. Lett.* **A 71** 146
- [10] Yu W-L and Zhao M-G 1988 *Phys. Rev.* **B 37** 9254
- [11] Zhao M-G, Du M-L and Yu W-L 1986 *Reprint IC/86/303*, International Center for Theoretical Physics, Trieste, Italy
- [12] Veremeichik T F, Grechusnikov B N, Varina T M, Sviridov D T and Kalinkina I N 1975 *Sov. Phys.-Crystallogr.* **19** 742
- [13] Euler F and Bruce J A 1965 *Acta Crystallogr.* **19** 971
- [14] Hodges J A 1974 *Proc. 18th Ampère Congr. (Nottingham)* p 153
- [15] Yogurtch Y K, Miller A J and Saunders G A 1980 *J. Phys. C: Solid State Phys.* **13** 6585
- [16] Zheng W-C 1989 *Phys. Status Solidi* **b 151** K145
- [17] Serway R A, Marshall S A and Robinson R B 1973 *Phys. Status Solidi* **b 56** 319