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The methods of determining the spin–lattice coupling coefficients G_{11} and G_{44} from the formulae for zero-field splitting

Wen-Chen Zheng

Centre of Theoretical Physics, CCAST (World Laboratory), Beijing, and Department of Material Science, Sichuan University, Chengdu 610064, People's Republic of China

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Abstract. In this paper the simple correlations between the spin–lattice coupling coefficients G_{11} and G_{44} and the axial (tetragonal and trigonal) crystal-field splittings have been established. According to the correlations, the methods of calculating the coefficients G_{11} and G_{44} from the formulae for zero-field splitting, which are easier to use than the usual correlations obtained directly from the strain tensor elements, are given. As an example, the analytic expressions of G_{11} and G_{44} for S-state ions in cubic crystals are obtained from two distinctive perturbation schemes based on the spin–orbit coupling mechanism. It can be found that the formulae for G_{44} obtained by Yu and Zhao from the same two schemes are not correct. The reason is perhaps that they confuse the actual shear strains e_{ij} $(i \neq j)$ with the strain tensor elements. The values of G_{44} for Mn^{2+} ions in MgO and CaO crystals are calculated. On comparison with the experimental results, it can be seen that our results are better than those of Yu and Zhao.

The spin-lattice coupling coefficients obtained from the uniaxial stress dependence of EPR spectra can provide knowledge of the direct spin–lattice relaxation time T_1 and the state of internal stress of a crystal; more importantly, they can also serve to elucidate the microscopic mechanisms of zero-field splittings. Therefore, in the past few decades, a considerable amount of theoretical work has been done on their microscopic origins [1–4]; in particular, the recent work of Yu and Zhao [4] from two distinctive perturbation schemes (scheme I was first suggested in [1]) based on the spin–orbit coupling mechanism. However, there is still some confusion about this problem and no simple method for obtaining the spin–lattice coupling coefficients from the formulae for zero-field splitting. In this paper, we would like to give the simple correlations between the coefficients G_{11} and G_{44} in cubic symmetry and the formulae for zero-field splitting in tetragonal and trigonal fields and to use them to derive the analytic expressions of G_{11} and G_{44} for S-state ions. On this basis, the coefficients G_{11} and G_{44} for Mn^{2+} ions in MgO and CaO crystals have been calculated. It can be found that from the two perturbation schemes the formulae for G_{11} are the same as those obtained by Yu and Zhao, but the formulae for G_{44} given by Yu and Zhao are not correct and their calculated results of G_{44} for Mn^{2+} ions in MgO and CaO crystals are not in as good agreement with experiments as those in this work.

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With the application of stress P (>0) along the [001] direction of cubic crystals, the tetragonal distortions around the z axis are induced and the zero-field splitting D due to the distortions should be [2]

$$D = -\tfrac{3}{2}C_{11}P \tag{1}$$

where the sign on the right-hand side is different from that in [2] because of the different sign for stress P. So,

$$\mathrm{d}D/\mathrm{d}P = -\tfrac{3}{2}C_{11} = -\tfrac{3}{2}G_{11}(s_{11} - s_{12}) \tag{2}$$

where s_{ij} is the element of the compliance tensor.

On the contrary, the tetragonal distortion can be represented by the bonding angle α ($\neq\alpha_0$, where $\alpha_0 = 45°$ denotes the angle of cubic symmetry (figure 1)), and

$$\tan\alpha = R_\perp/R_\parallel = R_0(1 - s_{12}P)/R_0(1 - s_{11}P). \tag{3}$$

Then

$$\mathrm{d}\alpha/\mathrm{d}P = \tfrac{1}{2}(s_{11} - s_{12}). \tag{4}$$

From thermodynamic analysis, in the slightly tetragonal distortion from cubic symmetry, we have

$$\mathrm{d}D/\mathrm{d}P = (\partial D/\partial R)_{\alpha=\alpha_0}\partial R/\partial P + (\partial D/\partial\alpha)_{\alpha=\alpha_0}\partial\alpha/\partial P = (\partial D/\partial\alpha)_{\alpha=\alpha_0}\partial\alpha/\partial P. \tag{5}$$

From (2)–(5), it can be found that

$$-\tfrac{3}{2}G_{11}(s_{11} - s_{12}) = (\partial D/\partial\alpha)_{\alpha=\alpha_0}\tfrac{1}{2}(s_{11} - s_{12}) \tag{6}$$

or

$$G_{11} = -\tfrac{1}{3}(\partial D/\partial\alpha)_{\alpha=\alpha_0}. \tag{7}$$

Similarly, when the stress P is along the [111] direction of cubic crystals, the trigonal distortion is induced; then

$$\mathrm{d}D/\mathrm{d}P = -C_{44} = -G_{44}s_{44}. \tag{8}$$

For the trigonal distortion β ($\neq\beta_0$, where $\beta_0 = 54.74°$, the bonding angle of cubic symmetry),

$$\mathrm{d}\beta/\mathrm{d}P = (\sqrt{2}/6)s_{44}. \tag{9}$$

Similar to the tetragonal symmetry, we have

$$G_{44} = -(\sqrt{2}/6)(\partial D/\partial\beta)_{\beta=\beta_0}. \tag{10}$$

It may be seen that the spin–lattice coupling coefficients G_{11} and G_{44} denote the simple correlations between the axial (tetragonal and trigonal) field splitting D and the angle distortions (tetragonal and trigonal), respectively. So, if the formulae for zero-field splitting in the tetragonal and trigonal symmetries have been obtained, the coefficients G_{11} and G_{44} can be calculated very easily. The method is simpler than the usual calculation directly from strain tensor elements and is applicable to all d^n ions and various mechanisms that contribute to zero-field splitting.

As an example, let us discuss the S-state ions. Many workers think that the spin–orbit coupling mechanism is of importance for zero-field splitting [5–8]. From the two distinctive perturbation schemes based on this mechanism, we have, in tetragonal symmetry [8]

$$D = -(\sqrt{5}/12)\xi^2(2P_{\alpha\alpha} - P_{\alpha\beta})P_{\alpha\gamma}B'_{40} \qquad \text{(scheme I)} \tag{11}$$

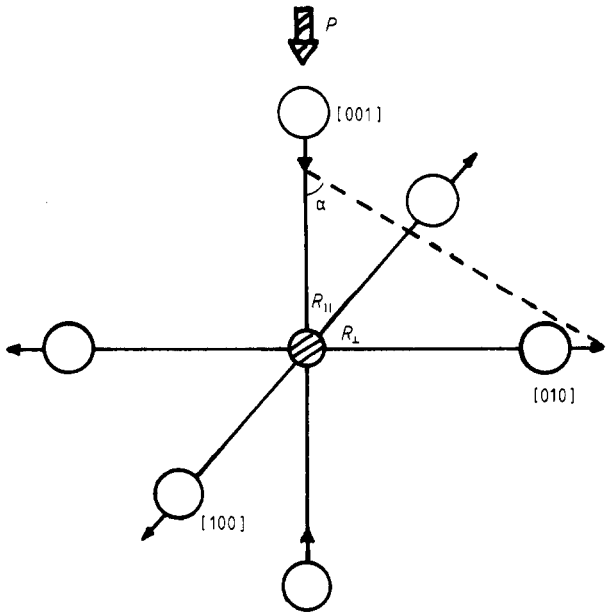

Figure 1. Displacements of six neighbouring ligands by stress along the [001] direction.

$$D = -(3\xi^2/70P^2D)(B_{20}^2 + 21\xi B_{20}) - (\xi^2/63P^2G)(5B_{40}^2 - 14B_{44}^2) \quad \text{(scheme II)} \qquad (12)$$

and, in trigonal symmetry [8],

$$D = (\sqrt{5}\xi^2/63)(7P_{\alpha\alpha} + 4P_{\alpha\beta})P_{\alpha\gamma}B'_{40} - (3\sqrt{5}/14)\xi^2 P_{\alpha\beta}P_{\alpha\gamma}B_{20} \quad \text{(scheme I)} \qquad (13)$$

$$D = -(3\xi^2/70P^2D)(B_{20}^2 + 21\xi B_{20}) - (\xi^2/126P^2G)(10B_{40}^2 - 7B_{43}^2) \quad \text{(scheme II)} \qquad (14)$$

where the crystal-field components B_{kq} are relative to the bonding angle α or β. According to (7), (10) and (11)–(14), the simple calculations show that

$$G_{11} = -(10\sqrt{5}/3)\,\xi^2 D_q(2P_{\alpha\alpha} - P_{\alpha\beta})P_{\alpha\gamma} \quad \text{(scheme I)} \qquad (15)$$

$$G_{11} = (400/3)(D_q^2\xi^2/P^2G) - (18/5)\xi^3 ee'\langle r^2\rangle/P^2DR^3 \quad \text{(scheme II)} \qquad (16)$$

and

$$G_{44} = (\sqrt{5}/7)\xi^2[7D_qP_{\alpha\alpha} + (4D_q + 3ee'\langle r^2\rangle/R^3)P_{\alpha\beta}]P_{\alpha\gamma} \quad \text{(scheme I)} \qquad (17)$$

$$G_{44} = -20D_q^2\xi^2/P^2G + (9/5)\xi^3 ee'\langle r^2\rangle/P^2DR^3 \quad \text{(scheme II).} \qquad (18)$$

Comparing our results with those of Yu and Zhao [4]† calculated from strain tensor elements by using he same perturbation schemes, it can be realised that, for G_{11}, our results are the same as those of Yu and Zhao for the two schemes but, for G_{44}, our results are half theirs. The reason is perhaps that, in their calculation, they confused the actual shear strains e_{ij} $(i \neq j)$ with the strain tensor elements. In fact, the former is half the

† For G_{44}, there are some typographical and slight calculation errors in [4, 8], e.g. $9ee'\langle r^2\rangle/R^3$ in (2) of [4] should read $6ee'\langle r^2\rangle/R^3$.

Table 1. Comparison of the coefficient G_{44} per unit strain for Mn^{2+} ions.

	MgO		CaO	
	Scheme I	Scheme II	Scheme I	Scheme II
G_{44} (cm^{-1}), this work	−0.21	−0.27	−0.09	−0.09
G_{44} (cm^{-1}), [4]	−0.41	−0.53	−0.17	−0.18
G_{44} (cm^{-1}), experiment	−0.31 [2]		−0.10 [10]	

latter. This can be supported by the following fact. In the work of Yu and Zhao, the formula for G_{44} in scheme II is equal to that for G_A^2, the spin–lattice coupling constant in D_{3d} symmetry [7]. When the hydrostatic pressure or the stress along the C_3 axis is applied to a crystal with D_{3d} symmetry, an additional zero-field splitting ΔD is induced which may be written

$$\Delta D = G_A^1(e_{xx} + e_{yy} + e_{zz}) + G_A^2[e_{zz} - \tfrac{1}{2}(e_{xx} + e_{yy})] \tag{19}$$

where, similar to G_{44}, G_A^2 also denotes the correlation of D with the bonding angle β [9]. However, G_A^2 is only related to the strain tensor elements e_{ii} which is the same as the actual strain. Obviously, when $\beta = \beta_0$, $G_A^2 = -(\sqrt{2}/3)\partial D/\partial\beta$ [9]†, which is not equal to the G_{44} but twice G_{44}.

Using the same parameters D_q, B, C, ξ, $P_{\alpha\alpha}$, $P_{\alpha\beta}$ and $P_{\alpha\gamma}$ as in [4], the coefficients G_{11} and G_{44} for Mn^{2+} ions in MgO and CaO crystals are calculated. Evidently, the values for G_{11} are the same as those obtained by Yu and Zhao. The results for G_{44} are shown in table 1. It can be seen that our results are closer to the experimental values than are those obtained by Zu and Zhao and can be regarded as more reasonable. Clearly, the method would be effective for other d^n ions, such as F-state ions. The study of other ions is in progress.

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† In my previous paper [9], $G_A^2 \simeq -\frac{1}{2}\partial D/\partial \ln\beta$.