On how to decide the relative importance of various mechanisms that contribute to the zero-field splitting using the ratio $(G_A^1)/D$

COMMENT

On how to decide the relative importance of various mechanisms that contribute to the zero-field splitting using the ratio G_A^1/D

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Abstract. In this Comment we will show that the ratio G_A^1/D denotes the value of n if we assume $D \simeq aV^n$. Hence, comparison between the theoretical and experimental values for the ratio G_A^1/D cannot be used to decide the relative importance of the various mechanisms that contribute to the zero-field splitting D because the value of D is dependent not only on n (i.e., G_A^1/D), but also on the value of a.

It is well known that the theoretical explanation of the zero-field splitting (ZFS) of ${}^6S$-state ions in crystals is very complex and difficult because there are many mechanisms that contribute, such as the BO mechanism [1], the spin–orbit coupling mechanism [2], the SS mechanism [3], the SS–SO mechanism [2], the overlap and covalency mechanism [4] and the ODS mechanism [5]. In fact, for simplicity, certain assumptions and approximations have to be made in the general calculation of the splitting D. It is, therefore, very important to find a method for deciding the relative importance of the various mechanisms for the splitting D.

Recently, Yu and Zhao [6] suggested a way of studying this problem. They are of the opinion that the spin–lattice coupling constant G_A^1 is proportional to the axial ZFS D for a ${}^6S$-state ion in D_{3d} symmetry, and hence that the comparison between the theoretical and experimental values for the ratio G_A^1/D can be used to decide the relative importance of various mechanisms. However, physical reasons to show why this method is valid are not clearly given and its reliability and applicability are doubtful. In this Comment we will show that although we do not reject the view that the spin–orbit coupling mechanism is dominant, the method given by Yu and Zhao is not effective in deciding the relative importance of various mechanisms—in particular, for the DOS, SS and SS–SO mechanisms.

From thermodynamic analysis, in trigonal symmetry, we have

$$\frac{\partial D}{\partial P} = \frac{\partial D}{\partial \ln R}\frac{\partial \ln R}{\partial P} + \frac{\partial D}{\partial \ln \alpha}\frac{\partial \ln \alpha}{\partial P} \tag{1}$$

$$\frac{\partial D}{\partial U} = \frac{\partial D}{\partial \ln R}\frac{\partial \ln R}{\partial U} + \frac{\partial D}{\partial \ln \alpha}\frac{\partial \ln \alpha}{\partial U} \tag{2}$$

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where U denotes the stress along the C_3 axis, R the bonding length and α the bonding angle.

When the surroundings are slightly distorted from cubic symmetry,

$$\partial \ln R/\partial P \simeq \tfrac{1}{3}(2S_{11} + 2S_{12} + 4S_{13} + S_{33}) \tag{3}$$

$$\partial \ln \alpha/\partial P \simeq \tfrac{1}{2}(S_{11} + S_{12} - S_{13} - S_{33}) \tag{4}$$

$$\partial \ln R/\partial U \simeq \tfrac{1}{3}(2S_{13} + S_{33}) \tag{5}$$

$$\partial \ln \alpha/\partial U \simeq \tfrac{1}{2}(S_{13} - S_{33}). \tag{6}$$

From the changes in the parameter D with pressure and stress [7], it follows that

$$\partial D/\partial P = G_A^1(2S_{11} + 2S_{12} + 4S_{13} + S_{33}) + G_A^2(S_{13} - S_{11} - S_{12} + S_{33})\dagger \tag{7}$$

$$\partial D/\partial U = G_A^1(2S_{13} + S_{33}) + G_A^2(S_{33} - S_{13}). \tag{8}$$

From equations (1)–(8), we have

$$G_A^1 = \tfrac{1}{3} \partial D/\partial \ln R = \partial D/\partial \ln V \tag{9}$$

$$G_A^2 = -\tfrac{1}{2} \partial D/\partial \ln \alpha. \tag{10}$$

It follows that the spin–lattice parameters G_A^1 and G_A^2 denote the correlations of D with R and α respectively. If we assume that $D = aV^n = aR^{3n}$, a simple calculation shows that

$$G_A^1/D = n. \tag{11}$$

From the above physical definition of the ratio G_A^1/D, it can be seen that a study of the ratio G_A^1/D (or n) cannot be regarded as an effective method for deciding the dominant mechanism and the relative importance of the various mechanisms that contribute to the ZFS D. The reasons are as follows. Firstly, assuming that there are m mechanisms that contribute to the ZFS D, i.e.

$$D = \sum_{i=1}^{m} D_i \tag{12}$$

and

$$D_i = a_i V^{n_i} \tag{13}$$

it follows that

$$nD = \sum_{i=1}^{m} n_i D_i \tag{14}$$

where n denotes the experimental value of G_A^1/D and n_i, the theoretical values for the various mechanisms.

If some mechanism D_1 dominates, we have $D \simeq D_1$, and hence $n \simeq n_1$. Hence the index n_1 (or G_A^1/D_1) of the dominant mechanism is indeed close to that obtained from experiment. However, this does not mean that the other values of n_i cannot be close to the experimental value because the value of D_i is dependent not only on n_i but also on the value of a_i. Even if the contribution of some mechanism is slight (i.e., $D_i \ll D$), it is

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† This equation is misprinted in [7] as

$$\partial D/\partial P = \tfrac{1}{3}[G_A^1(S_{11} + 2S_{12} + 4S_{13} + S_{33}) + G_A^2(S_{13} - S_{11} - S_{12} + S_{33})].$$

still possible to let $n_i \simeq n$, but with $a_i \ll a$, and hence to retain $D_i \ll D$. So, if there are several mechanisms in which all the indexes n_i are close to the experimental one, which mechanism is dominant. This cannot be determined using the method of Yu and Zhao.

Secondly, according to Yu and Zhao, the spin–orbit coupling mechanism dominates, and hence the experimental value of the ratio G_A^1/D should be close to $-\frac{10}{3}$, the theoretical prediction from the spin–orbit coupling mechanism. For example, the experimental value of G_A^1/D for $CaCO_3 : Mn^{2+}$ is -4.5 [7]. So, for a given mechanism, the closer to $-\frac{10}{3}$ the value of n_i, the more important the mechanism. However, this approach is neither appropriate nor reliable for ODS, SS and SS–SO mechanisms as will be seen from the following discussion.

For the ODS mechanism, it can be shown that D_{ODS} is proportional to $(A_0^2)^2$, so either the index n_{ODS} or the ratio G^1/D_{ODS} is equal to -2 because $A_0^2 \propto 1/R^3$. For the SS–SO mechanism, $n_{SS-SO} = -1$ because $D \propto B_{20}$, and for the SS mechanism, $n_{SS} = -1$ as pointed out by Yu and Zhao [6]. Hence the order of relative importance of the three mechanisms for the splitting D should be

$$\text{ODS} > \text{SS–SO} \simeq \text{SS}. \tag{15}$$

However, some researchers, including Yu and Zhao themselves [8], have pointed out that for the ^6S-state ions in trigonal symmetry

$$|D_{SS}| \gg |D_{SS-SO}| > |D_{ODS}|. \tag{16}$$

This can be seen from table 1. Obviously, the order of magnitude for the parameter D is entirely inconsistent with the relative importance of those mechanisms as given by Yu and Zhao's method. Hence the ratio G_A^1/D does not indicate the relative importance of the various mechanisms that contribute to the splitting D.

Table 1. The contributions of various mechanisms to the ZFS D of ^6S-state ions (in $10^{-4}\,cm^{-1}$).

	Symmetry	SO (4th)	SS	SS–SO	ODS	Expt
$YGaG : Fe^{3+}$ [8]	D_{3d}	-1476	165	32	19	-1320
$LuGaG : Fe^{3+}$ [8]	D_{3d}	-1632	180	34	22	-1290
$LuAlG : Fe^{3+}$ [8]	D_{3d}	-1236	126	24	12	-935
$YAlG : Fe^{3+}$ [8]	D_{3d}	-1308	131	26	12	-1053
$Al_2O_3 : Fe^{3+}$ [8]	C_{3v}	1207	-6	2	0	1679
$Al_2O_3 : Mn^{2+}$ [8]	C_{3v}	171	-2	$\simeq 0$	$\simeq 0$	194
$CdCl_2 : Mn^{2+}$ [11]	D_{3d}		-15.35		-4.85	<5
$Ca_5(PO_4)_3F : Mn$ (I) [2]	C_3	-543	104.1	30	-21.9	-472.5

In addition, it should be noted that apart from the errors inherent in the method described above, two problems that relate to the experimental value of G_A^1/D also seriously affect the reliability of the method.

(i) In the calculation of the experimental value of G_A^1, the elastic compliances in the vicinity of an impurity are usually assumed to be equal to those of the host crystal as shown in [7] for $CaCO_3 : Mn^{2+}$. However, the local elastic constants in the vicinity of an impurity are in fact different from those of the host, and the determination of the true local values is still a challenging problem [9, 10]. This may mean that the experimental value of G_A^1 deviates considerably from the theoretically expected value for some materials, and hence lead to the above method being unreliable.

(ii) In the various mechanisms for ZFS, only the static contribution related to the crystal-field components is taken into account theoretically. But the experimental value of D is made up of both static and vibrational contributions, i.e., $D = D_s + D_v$. If for some materials, the vibrational contribution D_v matches the static one, the experimental value of G_A^1/D may be about half of the value expected when only the static contribution is taken into consideration; this should make the ratio G_A^1/D of the ODS mechanism, but not of the spin–orbit coupling one, closer to that obtained from experiment, and lead the former to be more important to the ZFS D than the latter in accordance with the method of Yu and Zhao. Obviously, this is entirely incorrect, as many theoretical investigations show (see table 1).

In conclusion, although we do not reject the view that the spin–orbit coupling mechanism is the most important, we do hold that deciding the relative importance of various mechanisms that contribute to the ZFS by studying the ratio G_A^1/D is neither effective nor reliable.

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Reply by Yu Wan-Lun and Zhao Min-Guang

Firstly, we point out the following mistakes in Zheng's Comment.

(i) His equations (4) and (6), and therefore (10), are wrong. Let $L_{\|}$ and $L_{\perp}$ denote the crystal lengths parallel and perpendicular to the trigonal axis; we then obtain

$$\partial \ln L_{\|}/\partial P = S_{33} + 2S_{13} \qquad \partial \ln L_{\perp}/\partial P = S_{11} + S_{12} + S_{13}$$

$$\partial \ln L_{\|}/\partial U = S_{33} \qquad \partial \ln L_{\perp}/\partial U = S_{13} \tag{1}$$

and consequently

$$\partial \ln \tan \alpha/\partial P = S_{11} + S_{12} - S_{13} - S_{33} \tag{2}$$

$$\partial \ln \tan \alpha/\partial U = S_{13} - S_{33}. \tag{3}$$

Comparing these respectively with Zheng's equations (4) and (6), one finds that Zheng's equations cannot be correct unless the relationship

$$\partial \ln \tan \alpha/\partial X = 2 \partial \ln \alpha/\partial X \qquad X = P, U \tag{4}$$