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

(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 $L_\parallel$ and $L_\perp$ denote the crystal lengths parallel and perpendicular to the trigonal axis; we then obtain

$$\partial \ln L_\parallel/\partial P = S_{33} + 2S_{13} \qquad \partial \ln L_\perp/\partial P = S_{11} + S_{12} + S_{13}$$
$$\partial \ln L_\parallel/\partial U = S_{33} \qquad \partial \ln L_\perp/\partial U = S_{13} \tag{1}$$

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

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

holds. However, this is obviously wrong:

$$\frac{\partial \ln \tan \alpha}{\partial X} = (\tfrac{1}{2} \sin 2\alpha)^{-1} \frac{\partial \alpha}{\partial X} = \left(\frac{\alpha}{\sin 2\alpha}\right)\left(2\frac{\partial \ln \alpha}{\partial X}\right) \neq 2\frac{\partial \ln \alpha}{\partial X}. \tag{5}$$

So Zheng's equation (10) is basically wrong. Instead, its correct form is

$$G_A^2 = -\left(\frac{\partial D}{\partial \ln \tan \alpha}\right)_V. \tag{6}$$

(ii) The assumption $D = aV^n$ is somewhat incorrect. For instance, in D_{3d} symmetry, we have (Sharma 1970, 1971)

$$D_{SS} = AR^{-3}(3\cos^2\alpha - 1)$$

$$D_{ODS} = BR^{-6}(3\cos^2\alpha - 1)^2$$

in the point charge model. The volume V is now given as

$$V = CR^3 \cos\alpha \sin^2\alpha.$$

In these expressions, A, B and C are independent of R and α. Obviously

$$D_{SS} \neq aV^n \qquad D_{ODS} \neq bV^{n'}. \tag{7}$$

Similar cases occur for all other mechanisms.

(iii) The assumption $D = aR^{3n}$ does not in general hold. For the SO mechanism, we have

$$D_{SO} \doteq aB_{20} + b(B_{20})^2 + c(B_{40})^2 + d(B_{43})^2 = a'R^{-3} + b'R^{-6} + c'R^{-10} \tag{8}$$

in D_{3d} symmetry and in the point charge model (Yu and Zhao 1987). Equation (8) is suitable for weak fields. For strong fields, D_{SO} cannot be expanded in terms of B_{40} and B_{43}, so there is no expansion of the form of (8). Other mechanisms, such as ODS, SS, SS–SO, the covalency overlap (CO) and the relativistic (RE) mechanisms satisfy the relation $D = aR^{3n}$ well when one is omitting the vibration effect.

When the vibration effect is taken into consideration, none of the mechanisms satisfies this relation. The lattice vibration contributes to the zero-field splitting through each of the mechanisms. It is well known that

$$D_v = \tfrac{1}{2}\left\langle \sum_j (\partial^2 D_s/\partial Q_j^2)Q_j^2 \right\rangle \tag{9}$$

where Q_j are normal vibration modes. For a mechanism that satisfies $D_s = aR^{3n}$, we have from (9)

$$D_v = bR^{3n-2}. \tag{10}$$

Thus the total contribution is

$$D = D_s + D_v = aR^{3n} + bR^{3n-2}. \tag{11}$$

This cannot be expressed as $D = aR^{3n'}$, unless one of the two parts, D_s or D_v, can be omitted.

Therefore, equation (11) of Zheng, $G_A^1/D = n$, does not hold for the SO mechanism when we omit D_v and does not hold for any mechanism when we take D_v into account.

Secondly, Zheng may have misled readers in the following ways.

(i) Yu and Zhao (1987) proposed a method of identifying the most important (or the predominant) mechanism among the various mechanisms but did not suggest any method of deciding the order of importance of the mechanisms (i.e., which is the second, the third, the fourth etc most important), as described plausibly at the end of § 4 and in the conclusion of their original paper. In fact, we have identified the SO mechanism as being the most important for $Mn^{2+}:CaCO_3$, leaving the relative importance of the remaining mechanisms undiscussed. In his Comment, Zheng uses this method to decide the order of importance among the various mechanisms, leading to an incorrect result, and he consequently concludes that the method is not an effective means of identifying the most important mechanism. In this he may have confused readers.

(ii) Yu and Zhao's method of identifying the most important mechanism from the study of the ratio G_A^1/D *is* correct. Let us assume that m mechanisms contribute to D and that the ith is the most important:

$$D = D_1 + D_2 + \ldots + D_m \tag{12}$$

$$|D_i| \gg |D_j| \qquad j \neq i \tag{13}$$

$$|D_i| \gg |D_1 + D_2 + \ldots + D_{i-1} + D_{i+1} + \ldots + D_m|. \tag{14}$$

It follows from (12) that

$$G_A^1 = G_{A1}^1 + G_{A2}^1 + \ldots + G_{Am}^1 \tag{15}$$

because

$$G_A^1 = \left(\frac{\partial D}{\partial \ln V}\right)_{\tan \alpha} \tag{16}$$

(rather than (9) of Zheng). Dividing (15) by D and noting (13) and (14) we have

$$G_A^1/D \doteq G_{Ai}^1/D_i. \tag{17}$$

Equation (17) shows that if a mechanism dominates others it must be able to account for G_A^1/D as well. In fact, if a mechanism is most important at some stress state it should be so at all stress states. It is hard to see how the dominant mechanism becomes negligible and how a negligible mechanism changes to become the dominant one at another stress state. With the simple assumption $D = aR^{3n}$, (17) becomes $G_A^1/D \doteq n_i$.

The possibility raised by Zheng that there could be a mechanism that is negligible but which can account for G_A^1/D is most unlikely unless both the negligible and the dominant mechanism have the same or nearly the same index n. It is well known that the SO, CO and RE mechanisms are important, with indices $n_{SO} = -\frac{10}{3}$, $n_{RE} = -1$ and $n_{CO} = -\frac{5}{3}$, in the point charge model (Sharma 1983, Yu and Zhao 1988). D_{CO} and D_{RE} are opposite in sign. So even in the case where $G_A^1/D \doteq -1$ it is still very easy to identify which of them is the most important from the sign of D. The remaining mechanisms, such as ODS, SS and SS-SO, have been well known to be negligible for most of the cases, those in table 1 of Zheng serving as examples of this. Like SO, ODS is essentially the combined contribution of a crystal field and the spin–orbit coupling, but it includes the effect of the configuration interaction whereas SO is just within the d^5 configuration; hence usually $|D_{ODS}| \ll |D_{SO}|$. The conclusions $|D_{SS}| \ll |D_{SO}|$ and $|D_{SS-SO}| \ll |D_{SO}|$ can be observed from the fact that $|H_{SS}| \ll |H_{SO}|$ (see the review articles by Sharma 1983, Yu and Zhao 1988). Therefore it is reasonable to omit these three mechanisms for most cases. Nevertheless, one must take SO, CO and RE into account. The

remarkable difference in the values of the index n together with the fact that D_{CO} and D_{RE} are opposite in sign makes Yu and Zhao's method reliable.

(iii) Up to now, almost all of the studies in this area have been concerned with the static model: assuming $D = D_s$ or $D_v = 0$. Calculation of D_v is difficult, but its value can be estimated from experiments with temperature variation of D. For most cases, D_v is negligible compared with D_s, and so the static model works well in the calculation of spin-Hamiltonian parameters and their stress properties, as for $Mn^{2+}:CaCO_3$ (Serway 1971).

Importantly, it must be pointed out that 'a mechanism' in the literature refers just to the static model. For example, we have $D_{ODS} = a(A_2^0)^2$ (Sharma 1971); this just means the static model. For simplicity we denote this as $D_{ODS} = (D_{ODS})_s$. Any remark that a mechanism is important or negligible is meant to imply that we are talking about the static model and that it is in this model that the mechanism is important or negligible.

Now, Zheng refers to a mechanism as including both D_s and D_v. Accordingly, $D_{ODS} = (D_{ODS})_s + (D_{ODS})_v (\neq a(A_2^0)^2)$, and similarly for all other mechanisms. He is saying that when we include $(D_{ODS})_v$, then D_{ODS} as the sum of $(D_{ODS})_s$ and $(D_{ODS})_v$ could be important compared with $D_i = (D_i)_s + (D_i)_v$, $i \neq ODS$. This may of course happen 'for some materials', even excluding D_v. However, Zheng's list in table 1 then indicates that this should not happen. Here the following points must be mentioned. Firstly, the values given in Zheng's table 1 were obtained using the static model, i.e., $D_{ODS} = (D_{ODS})_s$, etc, so show only the relative importance in this model and do not show the importance of $D_{ODS} = (D_{ODS})_s + (D_{ODS})_v$ relative to other mechanisms. Secondly, the 'some materials' may not be those in his table 1, because this table does not cover all materials but only a few special cases. In fact, D_{ODS} may be greater in magnitude than D_{SO} in the static model. An example is provided by $CdCl_2:Mn^{2+}$, where D_{SO} is about $2 \times 10^{-4} cm^{-1}$ (Sharma 1970, 1971) and is smaller than D_{ODS} which is about $-5 \times 10^{-4} cm^{-1}$. This is obscured by Zheng in his table 1.

(iv) Zheng's first point is indeed a common problem in the study of the stress variation of spin-Hamiltonian parameters. The difference between the local compressibilities and the bulk ones may or may not be significant. In the case where the crystal has a simple structure and where the impurity and the substituted cation have the same charge and similar radii, the difference is most likely to be small and thus Yu and Zhao's method is applicable. Moreover it seems most unlikely for the difference to be several orders or more. Even in the case where the difference is great, the deduced G_A^1 is quite approximate and cannot be used for theoretical comparison, but sometimes it can be used to identify the most important mechanism, where $|n_{SO}|$ (3.33) is significantly greater than $|n_{RE}|$ and $|n_{CO}|$ (=1). For example, if the experimental value of G_A^1/D has a magnitude greater than n_{SO}, attribution to SO should be reasonable, as in the case of $Mn^{2+}:CaCO_3$.

We thus conclude that Zheng's main results are basically incorrect as is his conclusion concerning Yu and Zhao's method. Also the standpoint from which Zheng's Comment is made is incorrect. The study of the spin-Hamiltonian parameters of d^5 ions is a complicated one. To date no work has been published that takes all mechanisms into account and agrees with experiments; calculation of $(D_i)_s$ still remains a problem. A complete theory that takes into account all factors influencing the spin-Hamiltonian parameters is hard to establish. So authors have omitted some effects and proposed certain assumptions to simplify the problem. Thus their theories are not general theories; they are only applicable in the cases where such effects are negligible and such assumptions hold well. Workers who are applying a theory need to pay attention to the conditions on which the theory is established. However, one cannot argue that simply because a

theory omits some things and makes some assumptions it is unreliable. Further, Zheng has neither presented an experiment to show that D_v is not negligible nor proposed evidence to indicate the experimental value of G_A^1 to be unusable for $Mn^{2+}:CaCO_3$. Zheng has not shown Yu and Zhao's work to be unreliable nor their conclusions to be incorrect.

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