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COMMENT

On determining crystal structure from EPR and optical measurements

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Abstract. In this Comment we will show that the methods of determining the crystal structure parameters from EPR and optical measurements advanced by Zhao and co-workers are not reasonable and not reliable because there are four problems in their methods. So, unless all these problems are solved in principle their methods are literally impracticable, i.e., these methods cannot be used to derive crystal structure parameters with the same precision and accuracy as using the x-ray crystallographic method, let alone achieving better results than that.

The determination of crystal structure by means of methods other than the x-ray diffraction technique is a very interesting and significant problem. Recently, Zhao and co-workers made some efforts on this subject and achieved something [1–5]. They suggest that crystal structure parameters can be determined from EPR and optical data. In some papers [3, 5] they even thought the results derived by their methods are more accurate than the x-ray data because the EPR zero-field splitting depends sensitively on the crystal structure. However, this opinion is groundless, questionable and provokes further discussion. Baur and Sharma [6] have pointed out that the structural parameters of MnF_2 and ZnF_2 derived by Yu and Zhao by fitting with EPR and optical experiments not only lack the support of a great deal of experimental and theoretical methods but also are not self-consistent, so their other similar results [1, 2, 7] have to be questioned as well, mainly because the formulae of zero-field splitting used by Yu and Zhao are incorrect. Therefore, to determine the accurate crystal parameters, their methods cannot be used. Subsequently, Yu and Zhao [3] admitted that the formulae were wrongly derived in their previous papers. However, they still think that this will influence the quantitative results only slightly and thus does not change the conclusions of their papers. Obviously, this view of theirs cannot be regarded as suitable and convincing. In this Comment we will show that even if the relevant formulae were not wrongly derived in their papers the methods of determining the structural parameters advanced by them are still impracticable and unreliable because there are the following four problems in their methods.

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(i) In order to determine the structural parameters Zhao *et al* [1–5] first established the relationship between the zero-field splitting and the crystal-field components. But, for a reasonable theoretical explanation of zero-field splitting at room temperature, both the static contribution related to the crystal-field components and the vibrational contribution resulting from the electron–phonon interaction must be taken into consideration [8–11] (even as the temperature approaches zero there still is the zero-point vibrational contribution to the splitting [12]). That is, for the splitting D ,

$$D = D_s + D_v. \quad (1)$$

So, it is not reasonable to think that the observed value of splitting D is due only to the static part D_s as shown in all of Zhao and co-workers' papers. Although in some cases the vibrational contribution to the splitting D is small, for example, 10% of the total splitting, the accuracy of the structural parameters determined from the EPR data should evidently decrease. The reason that these methods are more accurate than the x-ray technique, in the opinion of Zhao and co-workers, is that the parameter D depends sensitively on the crystal structure. Obviously, these methods are not comparable with the x-ray method in precision and reliability. So, the very precise values of structural parameters derived from their methods, such as $R = 2.7234 \text{ \AA}$, $\theta = 54.814^\circ$ for CdCl_2 [3], $R = 2.426 \pm 0.008 \text{ \AA}$, $\theta = 53.225 \pm 0.005^\circ$ for NiCl_2 [5], are unconvincing and unreliable. In fact, the electron–phonon interaction cannot be omitted in some materials studied by Zhao and his co-workers. For instance, Zheng [8] has pointed out that the vibrational contribution D_v cannot be omitted for $\text{CdCl}_2:\text{Mn}^{2+}$ and the temperature variation of the crystal structure for CdCl_2 obtained from the EPR data by Yu and Zhao is unreliable. For other materials, such as MnF_2 , $\text{ZnF}_2:\text{Mn}^{2+}$, $\text{CdCl}_2:\text{Ni}^{2+}$ and $\text{CaZnF}_4:\text{Mn}^{2+}$, no experiments on the temperature dependence of zero-field splitting D have been reported and the vibrational contribution D_v cannot be obtained. However, it does not follow that we can arbitrarily think that this contribution can be neglected. So, if the contribution due to electron–phonon interaction is not considered their methods are not reasonable.

(ii) The d orbital used to calculate the crystal components is an empirical d orbital or an approximation of a SCF d orbital as admitted by Zhao and co-workers [13]. In addition, according to the fitting procedure of Zhao and co-workers using the point-charge crystalline-field model and the empirical d orbital it can be seen that the average covalency factor N and electric dipole moment μ are very difficult to determine accurately and uniquely, and change usually within a certain range if we use only the two adjustable parameters N and μ to fit many optical absorption bands. For example, the parameters determined in a paper of Du and Zhao are $N = 0.947\text{--}0.954$ and $\mu = 0.081\text{--}0.088 eR$ [4], while in another paper of Yu and Zhao they are $N = 0.9523$, $\mu = 0.078 eR$ [14] from the same d–d transitions in cubic $\text{MgO}:\text{Cr}^{3+}$. Similar cases can also occur in other materials. So, from the same parameter D and different values of N and μ , the structural parameters determined from their methods are not the same, as has been pointed out in [15] for $\text{Cr}^{3+}\text{--V}_c$ centre in MgO . Furthermore, in fitting with the d–d transitions they often used the cubic approximation to determine the values of N and μ in spite of the real local symmetry. Obviously, all the above approaches would bring about some errors and uncertainty in the determination of structural parameters.

(iii) In their methods the paramagnetic ions are usually used as probes to determine the structural parameters of a diamagnetic host. Although paramagnetic ion probes are extensively used in the studies of local symmetry and phase transition of a diamagnetic host [16–18], the method is unreliable and inaccurate in determining the structural

parameters and some properties, such as compressibility and thermal expansion coefficient, for a diamagnetic host because the structural parameters and local properties in the vicinity of an impurity indeed differ from those of host crystals in cases of valence and/or size mismatch [19–22]. The determination of these real local values is still a challenging problem [19, 23]. In the theoretical explanations of EPR and optical spectra the local geometries are often assumed to be the same as the host ones. However, this is only an assumption and approximation and not actually so. In fact, many workers have pointed out that the true impurity–ligand distance is not the same as that corresponding to the perfect lattice in the case of substitutional impurities. For instance, Moreno and Barriuso have shown that the values of the $\text{Mn}^{2+}\text{--F}^-$ distance, R , for Mn^{2+} in cubic fluoroperovskites, alkali fluorides [24], CdF_2 , CaF_2 and BaF_2 lattices [25] and also in PbF_2 crystal [26] are significantly different from those of host crystals from the isotropic superhyperfine constants. This conclusion is also supported by the EXAFS measurements for $\text{KZnF}_3:\text{Mn}^{2+}$ and $\text{RbCdF}_3:\text{Mn}^{2+}$ crystals [24]. On the other hand, the structural parameters of the $[\text{MX}_n]$ cluster formed by the substitutional impurity M and the n nearest anions X cannot be regarded as those of the isomorphous MX_m crystals as treated by Huang [5] in determining the crystal parameters of NiCl_2 from the $[\text{NiCl}_6]$ cluster in $\text{CdCl}_2:\text{Ni}^{2+}$. Even though CdCl_2 and NiCl_2 have the same crystal structure and approximately equal lattice parameters, the optical spectra of $\text{CdCl}_2:\text{Ni}^{2+}$ are indeed different from those of NiCl_2 [27–29]; this denotes that the structural parameters of the $[\text{NiCl}_6]$ cluster in CdCl_2 cannot be used as accurate values in a NiCl_2 crystal. Moreover, MgCl_2 and CdCl_2 have the same crystal structure and similar lattice parameters as MnCl_2 [30], but the zero-field splitting D for Mn^{2+} in CdCl_2 and MgCl_2 are not the same [31]. The question is, which one should be used to determine the accurate crystal parameters of MnCl_2 ? This obviously cannot be answered. So, the above point of view is not reasonable either.

(iv) It is more important that their methods must be based on the data of x-ray techniques and other methods, i.e., they can determine only some of the crystal parameters, otherwise they will raise some uncertainty, because the number of zero-field splittings is often less than the number of structural parameters to be determined. For example, for NiCl_2 crystal, only N and μ/eR can be determined from the model of Zhao *et al* [32]. By adjusting μ and R so that μ/eR remains unchanged, we can obtain a series of values of μ and R and then determine the values of θ as well from the unique zero-field splitting D . Which group of R and θ is correct? This obviously cannot be ascertained by the methods of Zhao and co-workers. A similar case also occurs in the crystals of MnF_2 and $\text{ZnF}_2:\text{Mn}^{2+}$. There are three structural parameters R_{\parallel} , R_0 and φ (or a , c and x) but only two zero-field splitting parameters D and E in them [2, 6]. In addition, the crystal parameters are also difficult to obtain accurately from optical measurements on account of the above reason (ii) even if the real local symmetry is considered. In fact, all the structural parameters determined by Zhao and co-workers are suggested by the x-ray results. So their methods are not effective in determining the crystal parameters unless some of the crystal parameters are given from other methods.

Finally, in passing, the recent work of Chen and Zhao [33] about the theoretical explanation of spin-Hamiltonian parameters for $\text{ZnF}_2:\text{Ni}^{2+}$ and NiF_2 should be studied. It is worth noticing that both the calculated EPR values from the sharply contrary structural parameters (one is an apically elongated and another an apically compressed coordination octahedron) given by Stout and Reed [34] and by Baur [35, 36] respectively are consistent with the observed values. This shows, conversely, that the methods of

Zhao and co-workers are not able to determine which group is correct, let alone produce concrete and more accurate data from them.

From the discussion above, the methods of Zhao and his co-workers are impracticable and unreliable. Only when the four problems have been solved to a certain extent can their methods be used to determine the crystal parameters roughly and approximately. They cannot even be regarded as comparable with the x-ray method in precision and accuracy, far less as improving upon it.

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Reply by Zhao Min-Guang

The conclusions drawn by Zheng are incorrect, because they are based on incorrect conclusions of three studies (quoted as references [8], [15] and [21] in Zheng's Comment) and on misunderstandings about the works of Zhao and co-workers. Before pointing out the misunderstandings, we analyse several incorrect points made in Zheng's previous works.