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Reply to `On determining crystal structure from EPR and optical measurements'

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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.

Zheng's work on the compressibility of α-$LiIO_3:Cr^{3+}$ [1], suffers from the simplicity of the mathematics. He said there that 'under pressure, we have

$$R = R_1[1 + (\partial \ln R/\partial P)_{V,T}P] \qquad \alpha = \alpha_1[1 + (\partial \ln \alpha/\partial P)_{V,T}P]$$

where R_1 and α_1 are the bonding length and the bonding angle at normal temperature and pressure respectively', and gave in his table 2 the formula $(\partial \ln R/\partial P)_{V,P} = -10.33 \times 10^{-4}\,\mathrm{kbar}^{-1}$. The expression for R is obviously wrong, because $R_1(\partial \ln R/\partial P)P$ does not have the same units as R. There is a similar problem with the expression for α. Furthermore, kbar^{-1} cannot serve as the unit for $\partial \ln R/\partial P$. Therefore all conclusions based on these formulae are highly questionable. For example, Zheng obtained (his equation (18))

$$(\partial \ln a/\partial P)_{V,T} = (1 + f)(\partial \ln a/\partial P)^{\mathrm{h}}_{V,T}$$

$$(\partial \ln c/\partial P)_{V,T} = (1 - f)(\partial \ln c/\partial P)^{\mathrm{h}}_{V,T}$$

where $f = 0.439$. One would consequently have $a = C(a_{\mathrm{h}}^{1+f})$ and $c = C(c_{\mathrm{h}}^{1+f})$. The fact that $a = a_{\mathrm{h}}$ and $c = c_{\mathrm{h}}$ for $f = 0$ leads to $C = 1$ and to

$$a = a_{\mathrm{h}}^{1.439} \qquad c = c_{\mathrm{h}}^{0.561}$$

where a, c, a_{h} and c_{h} are the unit-cell dimensions. This is incorrect because the LHS and RHS are in different units.

The conclusion of the work on $MgO:Cr^{3+}\,V_c$ centres [2] is wrong because Zheng has misunderstood the model suggested by Watkins, as pointed out by Du and Zhao [3]. The calculated value for $(\partial D/\partial T)_s$ of $CdCl_2:Mn^{2+}$ given in [4] was incorrect as pointed out by Yu [5]. It is opposite in sign to previous values calculated by Yu and Zhao [6] and by Sharma [7] and we have been unable to reach the sign Zheng gave by any method or model. These errors in Zheng's work undermine the basis of his Comment.

We now turn to replying directly to Zheng's Comment. Firstly, we point out that the vibration effect is usually negligible in determining the local structure parameters. It is well known that the real bond distances and angles of a crystal containing impurities are different from those of the host lattice. They can be measured by EXAFS experiments if a large number of impurities are present [8]. Indirect methods of determining them from experimental EPR parameters, such as the cubic zero-field splitting (ZFS) a [9], the superhyperfine constant A_s [8] and the low-symmetry ZFS parameters D and E [10, 11], have been shown to be highly useful and reliable as the results deduced are consistent with experiments [8, 9]. The basic idea of this method is that the EPR parameters depend sensitively on the local structure. It should be pointed out, however, that all of the methods are based on approximate theories [8] and even on empirical models [9–11]. Some complex effects that do not significantly influence the final results have been omitted in published work, such as the electron–phonon coupling that was strongly stressed in Zheng's Comment. In fact, it is difficult to assess the contribution of the electron–phonon coupling to the EPR parameters, especially for substitutional ions. However, it is accepted that this contribution is much smaller than the geometrical contribution for most cases. In the work of Shrivastava [12], which was quoted in support of Zheng's first argument, this contribution was estimated to be less than 6% of the total value in the temperature range 0–600 K, for a value of a of $ZnS:Mn^{2+}$. A similar case occurs for the axial centre of $MgO:Cr^{3+}$—see the work of Manoogian [13], mentioned by Zheng. Another piece of work quoted in support of Zheng's first argument is one of his own studies we have already shown to be dubious [4]. In that work, he calculated the static contribution, $(\partial D/\partial T)_s$, and obtained a value of $1.62 \times 10^{-5}\,\mathrm{cm}^{-1}\,\mathrm{K}^{-1}$, for

$CdCl_2:Mn^{2+}$. Subtracting this from the experimental value $(\partial D/\partial T) = -1 \times 10^{-5}\,cm^{-1}\,K^{-1}$, he obtained (incorrectly) $(\partial D/\partial T)_v = -1.05 \times 10^{-5}\,cm^{-1}\,K^{-1}$ as the vibration contribution, and arrived at the conclusion that the vibration effect is important in this system. However, the calculated value for $(\partial D/\partial T)_s$ is incorrect [5]. In fact, one always obtains a negative value for this quantity not a positive value no matter what method or model is used. For instance, a value of $-0.17 \times 10^{-5}\,cm^{-1}\,K^{-1}$ has been calculated by Sharma [7] in the lattice summation model of the crystal field (CF). Further, it is a simple matter to see that $|(\partial D/\partial T)_s| < |(\partial D/\partial T)_v|$ cannot show that $|D_s| < |D_v|$.

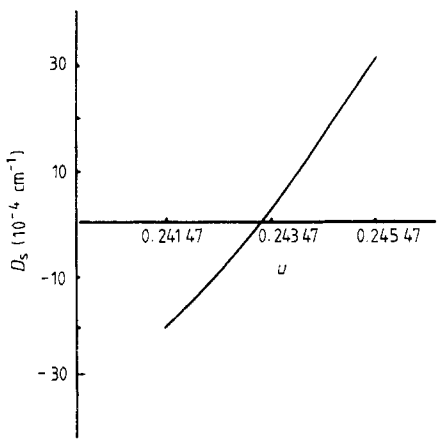

Figure 1. D_s of $CdCl_2:Mn^{2+}$ as a function of u.

Figure 1 gives an example to show that the vibration contribution can be omitted in the determination of the local structure parameters from the ZFS even when D_v is comparable in magnitude with D_s. From the figure one can see a sensitive dependence of D_s on the unit-cell dimension u. When u changes from 0.24147 to 0.24547, an increase of 0.004, D_s goes from -20×10^{-4} to $+32 \times 10^{-4}\,cm^{-1}$. At 300 K, $D(\text{exp}) \doteq 3 \times 10^{-4}\,cm^{-1}$ and one obtains $u = 0.24347$ under the assumption that $D(\text{exp}) = D_s$ (or $D_v = 0$) and $u = 0.2440$ for $D_v = -3 \times 10^{-4}\,cm^{-1} = -D(\text{exp})$. The values of u only differ by 0.0005; thus the result, $u = 0.2435 \pm 0.0005$, given in [6] is reasonable, even taking the vibration effect into account. Furthermore, when this result is compared with the experimental x-ray value $u = 0.25 \pm 0.01$, one sees a good agreement and better accuracy.

We have shown that the inclusion of the vibration effect does not significantly influence the final results for local structure parameters, even in the cases where the contribution of this effect to the EPR parameters is comparable with the static contribution for some situations. In particular, for $d^{1,9}$ ions, the vibrational contribution is negligible compared with the static one, as pointed out by Abagam and Bleaney [14]. For example, the g-factors for the d^9 ion can be written as

$$\begin{aligned} g_{xx} &= 2 - (2\lambda/\Delta_2)(\cos\tfrac{1}{2}\varphi + \sqrt{3}\sin\tfrac{1}{2}\varphi)^2 \\ g_{yy} &= 2 - (2\lambda/\Delta_2)(\cos\tfrac{1}{2}\varphi - \sqrt{3}\sin\tfrac{1}{2}\varphi)^2 \\ g_{zz} &= 2 - (8\lambda/\Delta_1)\cos^2\tfrac{1}{2}\varphi \end{aligned} \tag{1}$$

where φ is a function of time due to the oscillation; Δ_1 and Δ_2 are the energies of the excited states d_{xy} and d_{zx}, respectively. At high temperature, since the vibrational frequency is large compared with the frequency at which EPR is observed, only time-averaged values are observed. Hence,

$$\langle \cos^2 \tfrac{1}{2}\varphi \rangle = \langle \sin^2 \tfrac{1}{2}\varphi \rangle = \tfrac{1}{2} \qquad \langle \cos \tfrac{1}{2}\varphi \sin \tfrac{1}{2}\varphi \rangle = 0. \tag{2}$$

Neglecting the difference between Δ_1 and Δ_2 gives

$$g_{xx} = g_{yy} = g_{zz} = 2 - 4\lambda/\Delta = (g_{\parallel} + 2g_{\perp})/3. \tag{3}$$

This is just the result of static crystal-field (SCF) theory. Sugano and co-workers [15] have pointed out that the energies of the transition-metal ions depend only on the average bond distances. This is to say, for instance, that $Dq \propto R_0^{-n}$, $n > 0$, where $R_0 = \langle R \rangle$ is the distance in the static configuration. However, one has to regard R_0^{-n} as $\langle R^{-n} \rangle$ when dealing with the lineshape and related problems.

Secondly, the method developed by Zhao and co-workers is based on the CF theory and involves parameters such as N and μ (dipole moment) that should be adjusted from optical spectra. Owing to the uncertainties of optical experiments and also to the approximations of the CF theory, these parameters cannot be uniquely determined—but this will not significantly influence the local structure parameters deduced, as has been shown by Du and Zhao [3].

Thirdly, Zheng seems to discuss the difference between the host lattice and the lattice having impurities, in his third point, but his idea seems to be illogical. It must be pointed out that (i) the optical and EPR parameters are closely related to the local geometries of the clusters; (ii) for the crystal containing impurities, the local geometry of the cluster differs from the host lattice; and (iii) the local structure parameters of the cluster are determined from the quantitative relationship between the local geometry and the optical and EPR parameters in our method. For $MgCl_2:Mn^{2+}$, $CdCl_2:Mn^{2+}$ and $MnCl_2$, since their ZFSs are different [16], three sets of structure parameters may be correspondingly deduced. So Zheng's question 'which one should be used to determine the accurate crystal parameters of $MnCl_2$' does not arise. This just shows that the character of our method differs from that of the x-ray technique. The difference in the local structures of different clusters that are in host lattices possessing the same crystal structure can be studied. The local structure of a crystal containing an impurity differs from the host lattice, but this difference is expected to be small for most cases. Since the true local geometry of the cluster of impurities has not been determined for many crystals, the local structures are often assumed to be identical to the perfect lattices. This assumption is widely employed in the literature. Although the accuracy of the result will be influenced, one cannot say that this is not reasonable or is unreliable.

Fourthly, our method depends on x-ray data at two points. One is that the local symmetry is assumed to be unchanged when the impurity is substituted in. This has been verified by a large number of EPR experiments, although relaxations usually take place. Another point is that we assume the local structure around the impurity to be close to that of the host lattice and this is what is found by x-ray experiments. From the latter, the arbitrariness and indefiniteness are eliminated. This means that within the error range, a unique group of local structure parameters related to EPR and optical data can be obtained. It should be pointed out that Zheng's assertion that 'all the structure parameters determined by Zhao and co-workers are suggested by x-ray results' is so far from fact that all the results obtained are different from the x-ray data (although they are close, see the second point above). Some results have no x-ray correspondence, in

fact. For example, the x-ray technique cannot measure the local structure parameters of the Cr^{3+} V_c centres in MgO that have been determined, using the method of Zhao and co-workers, by Du and Zhao [3] and He and Du [17]. Noting that the local geometry of the cluster around the impurity and of the vacancy centres cannot be measured by x-ray experiments, the usefulness of this method is obvious.

Finally, it must be pointed out that the accuracy of our method depends not only on the theoretical model but also on the accuracy and completeness of optical and EPR data. For example, the magnitudes and the signs of the EPR parameters and the fine structures of optical spectra may be different for elongated or compressed octahedra. Thus, it is possible to apply this method in determining whether the Ni^{2+} cluster in ZnF_2 is elongated or compressed, provided that a wide range of EPR and polarised optical data are available. Obviously, this method cannot be negated on the basis of one incomplete work.

In conclusion, we hold Zheng's conclusion to be entirely incorrect. The method of determining the local structure parameters from the EPR data is available and the usefulness and the results are reliable. The exclusion of the vibration effect will not significantly influence the final results.

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