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## Superposition model analysis of $\text{Cr}^{3+}$ in sodium ammonium sulphate dihydrate

J Kuriata<sup>†</sup>, J M Baker<sup>‡</sup>, L Sadłowski<sup>†</sup>, I Stefaniuk<sup>†</sup> and T Bodziony<sup>†</sup>

<sup>†</sup> Instytut Fizyki, Politechnika Szczecińska, Aleja Piastów 17, 70-310 Szczecin, Poland

<sup>‡</sup> Oxford Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

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**Abstract.** This paper discusses the application of the superposition model of Newman to studies of local distortions around  $\text{Cr}^{3+}$  ions doped into sodium ammonium sulphate dihydrate. It is shown that local distortions and a model for the charge compensation mechanism can be derived from the standard use of the superposition model for two of the sites observed ( $\beta$  and  $\beta'$ ). The calculations were carried out for the spin Hamiltonian parameters measured at temperatures both above and below the phase transition detected at  $95 \pm 0.5$  K. It is shown that the phase transition induces a substantial decrease in the metal–ligand distance in  $\text{CrO}_6$  octahedra.

### 1. Introduction

The superposition model (SM) of Newman (see e.g. Bradbury and Newman 1967, Newman and Ing 1989) allows one to calculate, for a paramagnetic ion, the parameters of the spin Hamiltonian which describe the fine structure set up by interaction with ligands at known relative positions. It has often been applied in the reverse order to derive unique information about local distortions around paramagnetic ions doped into diamagnetic lattices. The applicability of the model to rare earth ions (especially those in the  $^8\text{S}_{7/2}$  ground state) has been verified, for example, by Newman and Urban (1972, 1975). The model was later applied to iron group ions such as  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  by Müller and Berlinger (1983) and Müller *et al* (1985).

However, its use for  $\text{Cr}^{3+}$  is still controversial because, as pointed out by Newman and Ing (1989), for  $\text{Cr}^{3+}$  it is incorrect to assume that effective spin operators  $S$  necessarily transform as  $R_3$  vectors, as was assumed in the formulation of the problem by Müller *et al*. Nevertheless, Newman and Ing concluded that the deductions of Müller *et al* were valid for the specific problem of local distortions around  $\text{Cr}^{3+}$  in the orthorhombic phase of  $\text{BaTiO}_4$ , even though somewhat incorrect basic assumptions were made about the formalism. It is clear that the superposition model has a semi-empirical character so that its range of application is still to be established by systematic experimental studies.

In our two previous papers (Baker *et al* 1995, Kuriata *et al* 1995) we have reported that  $\text{Cr}^{3+}$  ions doped into sodium ammonium sulphate dihydrate (SASD) form three different paramagnetic centres called  $\alpha$ ,  $\beta$  and  $\beta'$ . A superposition model analysis was carried out for centre  $\alpha$  assuming that it corresponds to  $\text{Cr}^{3+}$  at undistorted  $\text{Na}^+$  sites. The reasons for this assumption were given by Baker *et al* (1995), but primarily rely on the assumption that

the most abundant site in most crystals ( $\alpha$ ) is likely to be the site where  $\text{Cr}^{3+}$  substitutes for the cation. This analysis led us to two conclusions:

- (i) that there is no obvious correlation between the principal directions predicted by the model and the bond directions, as might have been expected for a site of low symmetry,
- (ii) that the calculated parameters were as much as an order of magnitude larger than those measured experimentally.

These observations implied the conclusion that the  $\alpha$  site is probably severely distorted from the  $\text{Na}^+$  site. No models were proposed for the  $\beta$  and  $\beta'$  sites, though several possible sites were suggested. There is an unfortunate error in table 1 of Baker *et al* (1995), which has been carried over into table 1 of Kuriata *et al* (1995); for the  $\beta$  and  $\beta'$  sites, but not for the  $\alpha$  site, the direction cosines  $l$  and  $m$  should be interchanged. This reassignment has been carefully checked by new comparison of EPR data and x-ray diffraction.

The nature of the ferroelectric phase transitions in  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and isomorphous  $\text{NaNH}_4\text{SeO}_4 \cdot 2\text{H}_2\text{O}$  has been the subject of many papers of which that by Aleksandrov *et al* (1978) seems to be most comprehensive. Based on the results of many experimental methods they were able to propose a semi-quantitative model, according to which the phase transition is of the mixed (trigger) type involving not only active ionic displacements in the  $\text{NaO}_6$  octahedra but also ordering processes of hydrogen bonds and tetrahedral groups.

This paper describes the results of our SM calculations carried out for  $\beta$  and  $\beta'$  centres assuming that they are formed by  $\text{Cr}^{3+}$  ions at  $\text{Na}^+$  sites and assuming that this substitution leads to both radial and angular distortions. The ionic displacements in the  $\text{CrO}_6$  octahedra during the ferroelectric phase transition are also estimated.

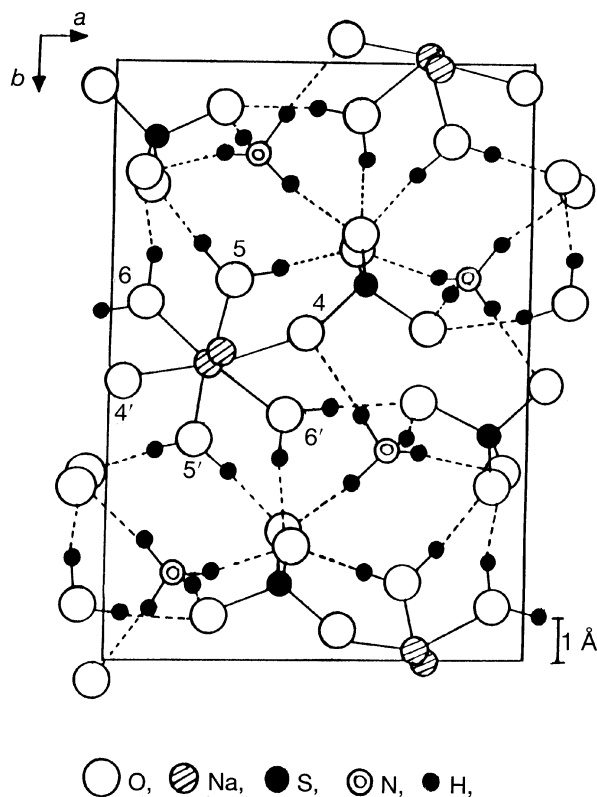
## 2. Crystal structure and the method of calculation

Although we have already, in our previous paper, described the crystal structure of SASD based on the detailed data given by Corrazzo *et al* (1967) and Aleksandrov *et al* (1978) it seems that for the convenience of the reader it is worthwhile repeating some important information which is relevant to this paper.

SASD and the isomorphous SASeD are orthorhombic with space group  $P2_12_12_1$  and four molecules in the unit cell in the paraelectric phase, and  $P2_1$  in the ferroelectric phase. The crystal structure of the former is shown in figure 1. The Na atoms are arranged very near the screw axis. Their coordination octahedra share opposite faces and form straight chains parallel to the  $c$  axis. A chain of  $\text{NaO}_6$  octahedra in pure crystals is shown in figure 2(a). The chains of  $\text{NaO}_6$  are interlaced with chains of  $(\text{NH}_4^+)-(\text{SO}_4^{2-})-(\text{NH}_4^+)$ . The two types of chain are linked by sharing one oxygen in the  $\text{SO}_4$  tetrahedra and hydrogen bonds. It is also important to note that, according to the data given by Aleksandrov *et al* (1978), the four water molecules in oxygen positions 5, 5', 6 and 6' are not exactly the same because those in positions 5 and 5' differ from those in positions 6 and 6' in that they have two so-called 'curved' bonds. The bond angle between H–O–H, and also bond lengths, are different for these two types of water molecule.

$\text{Na}-\text{O}(n)$  bond lengths and bond directions calculated from the crystallographic data of Corrazzo *et al* are given in table 1.

The computer program for calculations of the oxygen coordinates in  $\text{CrO}_6$  octahedra was based on the principal assumptions of the superposition model, and two additional conditions governing the starting parameters and the minimal metal–ligand distance imposed by the ionic radii of the ions involved.



**Figure 1.** The crystal structure of SASD viewed along [001].

**Table 1.** Ligand bond lengths and ligand bond directions for pure SASD. Direction cosines are relative to crystallographic axes [100], [010], [001].

Bond	Bond length (nm)	Bond direction			Spherical angles	
		$l$	$m$	$n$	$\varphi$ ( $^\circ$ )	$\vartheta$ ( $^\circ$ )
Na-O(6)	0.247	-0.518	-0.579	0.632	228.1	129
Na-O(5)	0.240	0.183	-0.804	-0.567	282.8	55.2
Na-O(4)	0.245	0.759	-0.314	0.571	337.5	125
Na-O(6')	0.242	0.632	0.430	-0.645	34.2	50
Na-O(5')	0.235	-0.081	0.655	0.749	97	138.5
Na-O(4')	0.238	-0.676	0.164	-0.718	157	44

In the superposition model of Newman it is assumed that the spin Hamiltonian parameters  $b_n^m$  can be expressed in the form:

$$b_n^m = \sum_i \bar{b}_n(R_i) K_n^m(\vartheta_i, \varphi_i) \quad (1)$$

where  $\bar{b}_n(R_i)$  are 'intrinsic' parameters depending only upon the type of ligand and its distance  $R_i$  from the paramagnetic ion,  $K_n^m(\vartheta_i, \varphi_i)$  are angular coordination factors tabulated

**Table 2.** Structural parameters for oxygen ligands obtained from the superposition model for centre  $\beta$  observed at room temperature.

Bond	Spherical angles ( $^\circ$ )		Distance (nm)
	$\varphi$	$\vartheta$	
Cr–O(6)	218(2)	110(2)	0.215(1)
Cr–O(5)	272(2)	32(2)	0.230(1)
Cr–O(4)	316(2)	110(2)	0.205(1)
Cr–O(6')	37(2)	70(2)	0.210(1)
Cr–O(5')	92(2)	148(2)	0.220(1)
Cr–O(4')	138(2)	70(2)	0.205(1)

**Table 3.** Structural parameters for oxygen ligands obtained from the superposition model for centre  $\beta'$  observed at room temperature.

Bond	Spherical angles ( $^\circ$ )		Distance (nm)
	$\varphi$	$\vartheta$	
Cr–O(6)	213(3)	110(3)	0.215(3)
Cr–O(5)	288(3)	48(3)	0.225(5)
Cr–O(4)	317(3)	135(3)	0.205(5)
Cr–O(6')	33(3)	74(3)	0.210(5)
Cr–O(5')	108(3)	140(3)	0.220(5)
Cr–O(4')	137(3)	49(3)	0.225(5)

**Table 4.** Comparison of the direction cosines of the measured principal axes of the  $\mathbf{D}$  matrix with the directions O( $n$ )–O( $n'$ ) deduced using SM for the  $\beta$  centre.

Ligand pairs	Direction cosines calculated from SM			Direction cosines measured experimentally		
	$l$	$m$	$n$	$l$	$m$	$n$
O(5)–O(5')	0.018(2)	–0.530(3)	0.843(3)	0.014(10)	–0.509(12)	0.861(11)
O(4)–O(4')	0.735(3)	0.564(3)	0.374(2)	0.743(11)	0.582(12)	0.332(11)
O(6)–O(6')	–0.667(3)	0.623(3)	0.406(2)	–0.670(12)	0.635(12)	0.386(11)

by Newman and Ing (1989), which are independent of the type of ligand and  $R_i$ , and the summation is carried out over all ligands.

The radial dependence of the  $\bar{b}_n(R_i)$  intrinsic parameter has been shown experimentally (see e.g. Newman and Urban 1972, Müller and Berlinger 1983) to follow the law:

$$\bar{b}_2(R) = -A(R_0/R)^{10} + B(R_0/R)^{13}. \quad (2)$$

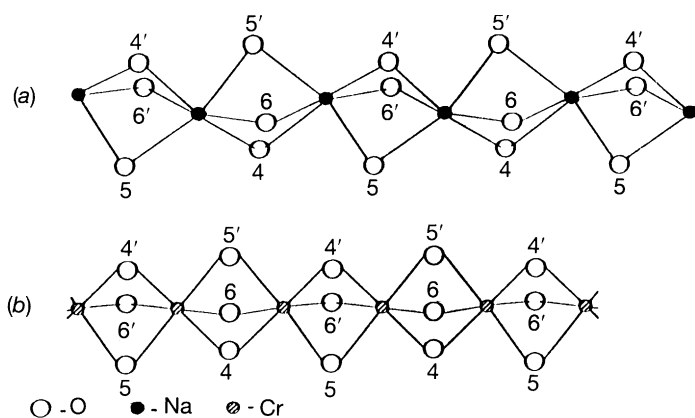
Equations (1) and (2) can be used to derive geometrical data about the ligand positions from EPR measurements if the three parameters  $A$ ,  $B$  and  $R_0$  can be established. However, this is not easy, because, as shown for example by Müller and Berlinger (1983) and Kuriata *et al* (1983), their determination requires precise measurements of EPR under uniaxial stress. Because we could not perform such experiments on the fragile SASD crystals doped with  $\text{Cr}^{3+}$ , we had to derive the values of  $A$ ,  $B$  and  $R_0$  by extrapolation of the results given by Müller and Berlinger to the case where  $\text{Cr}^{3+}$  substitutes for a monovalent ion. The values

**Table 5.** Comparison of the direction cosines of the measured principal axes of the **D** matrix with the directions  $O(n)-O(n')$  deduced using SM for the  $\beta'$  centre.

Ligand pairs	Direction cosines calculated from SM			Direction cosines measured experimentally		
	<i>l</i>	<i>m</i>	<i>n</i>	<i>l</i>	<i>m</i>	<i>n</i>
O(5)–O(5')	–0.21(1)	0.66(1)	–0.72(1)	–0.218(42)	0.681(31)	–0.700(36)
O(4)–O(4')	–0.53(1)	0.49(1)	0.68(1)	–0.548(34)	0.514(37)	0.659(32)
O(6)–O(6')	0.80(1)	0.51(1)	0.31(1)	0.808(25)	0.522(37)	0.275(42)

**Table 6.** The distances  $O(n)-Na^+-O(n')$  for pure material at room temperature and the distances  $O(n)-Cr^{3+}-O(n')$  calculated from the temperature dependence of the spin Hamiltonian parameters for the  $\beta$  centre and the superposition model.

Distance between	Pure crystal (nm)	$\beta$ centre (nm)		
		297 K	95 K	92 K
O(5)–O(5')	0.475	0.447(3)	0.435(3)	0.426(3)
O(6)–O(6')	0.489	0.433(3)	0.420(3)	0.411(3)
O(4)–O(4')	0.483	0.423(3)	0.410(3)	0.401(3)

**Figure 2.** Chains of oxygen octahedra (a) for pure SASD and (b) for a hypothetical chain in which all  $Na^+$  ions are replaced by  $Cr^{3+}$ .

thus found are given by Baker *et al* (1995) and they are:

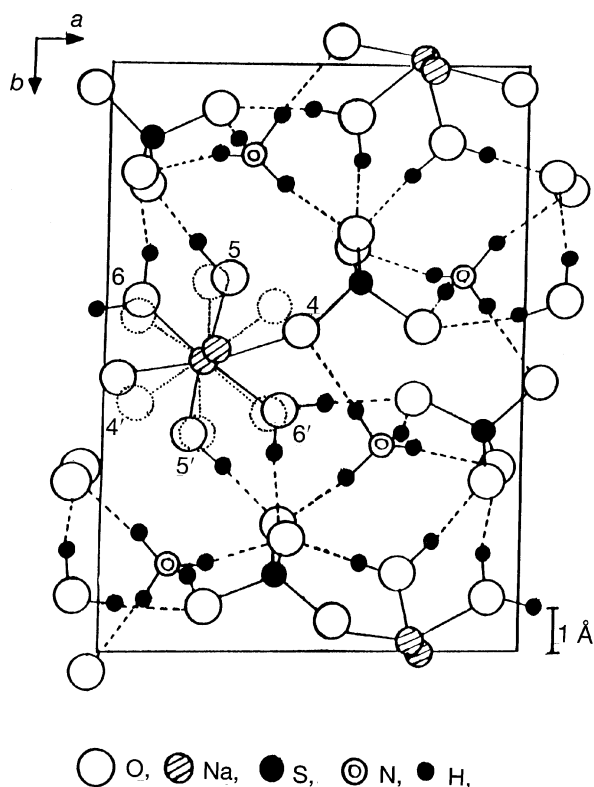
$$A = -7.3 \text{ cm}^{-1} \quad B = 5.3 \text{ cm}^{-1} \quad R_0 = 0.219 \text{ nm.}$$

The coordination factors used in this paper are taken from Newman and Ing (1989) and they are:

$$\begin{aligned} K_2^0 &= \frac{1}{2}(3 \cos \vartheta - 1) \\ K_2^2 &= \frac{3}{2} \sin \vartheta \cos 2\varphi. \end{aligned} \quad (3)$$

The spin Hamiltonian parameters were derived from the standard form:

$$H = \mu_B \mathbf{SgB} + \mathbf{SDS} \quad (4)$$



(a)

**Figure 3.** The models of charge compensation: (a) for centre  $\beta$  and (b) for centre  $\beta'$ . Dotted circles and lines denote ligand positions and bond directions respectively resulting from the proposed model of charge compensation.

with the relationship between the matrix elements of  $\mathbf{D}$  and  $b_n^m$  given by:

$$\begin{aligned} b_2^0 &= (3/2)D_{zz} \\ b_2^{\pm 1} &= (1/2)(D_{zx} \pm iD_{zy}) \\ b_2^{\pm 2} &= (1/4)(D_{xx} - D_{yy} \pm 2iD_{xy}) \end{aligned} \quad (5)$$

The computer program was written so that  $R_i$ ,  $\vartheta_i$ ,  $\phi_i$  parameters in equations (1) and (2), describing the spatial position of six oxygen ligands relative to  $\text{Cr}^{3+}$ , were adjusted for the best fit measured by least mean square deviation between the calculated values of  $b_n^m$  and those determined by diagonalization of (4). In order to make this calculation converge, two additional conditions were imposed:

- (a) the structure data given in table 1 were taken as a set of starting parameters,
- (b) a minimum metal–ligand distance of 0.196 nm was imposed based on knowledge of the ionic radii of  $\text{Cr}^{3+}$  and  $\text{O}^{2-}$ .

It is interesting that our calculations showed that the rms deviation between the calculated and measured spin Hamiltonian parameter was relatively insensitive to changes of  $R_i$ ; however, it was very sensitive to even small changes in  $\vartheta_i$  and  $\phi_i$ .

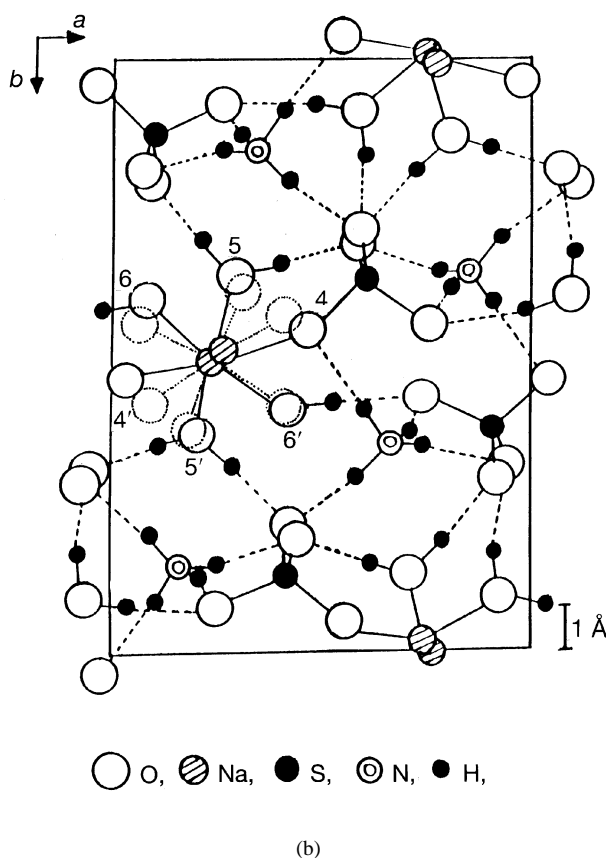


Figure 3. (Continued)

This may explain the failure of the earlier attempt to apply the superposition model to the interpretation of the spin Hamiltonian parameters for the  $\alpha$  centre by Baker *et al* (1995).

### 3. Results and discussion

The experimental data to be analysed have been given by Baker *et al* (1995) and Kuriata *et al* (1995). Following the method described above, oxygen ligand positions required to produce the observed fine structure were calculated for both  $\beta$  and  $\beta'$  centres at room temperature. The results of these calculations are given in tables 2 and 3. Based on the derived data we then inspected to see whether there exists a relation between principal directions of the  $\mathbf{D}$  matrix measured experimentally and those resulting from bond directions. The results are presented in tables 4 and 5.

Finally, we have repeated the same calculations at two temperature points just above and below the ferroelectric phase transition. The results are listed in table 6.

As can be seen by comparing table 1 with tables 2 and 3, the doping with  $\text{Cr}^{3+}$  leads to radial and angular distortions in the oxygen octahedra around  $\text{Cr}^{3+}$  substituting for  $\text{Na}^+$ . In order to visualize the effect of doping we constructed, based on the structure data given in



table 2, a hypothetical chain of octahedra in which all  $\text{Na}^+$  ions are replaced by  $\text{Cr}^{3+}$ . The comparison of this chain to that for pure SASD is shown in figure 2. The doping appears to lead to a more regular octahedral structure, a shortening of the chain along the  $c$  axis and there is some rotation of the octahedron as a whole which can be estimated from the data given in table 1 and 2 to be about  $10^\circ$ .

Incidentally, it is interesting to note that single crystals grown containing chromium are clearly flattened along the  $c$  axis in their morphology compared with that of the pure crystal. It may also be speculated that this more regular structure somehow stabilizes the crystal, causing the critical temperature of the phase transition determined using EPR ( $95 \pm 0.5$  K) to be less than that measured by dielectric measurements ( $101 \pm 1$  K) (Pepinsky 1959, Makita and Seikido 1965).

The data derived from our SM analysis also suggest a model for charge compensation when the monovalent  $\text{Na}^+$  ions are replaced by trivalent  $\text{Cr}^{3+}$  ions. It seems that the most probable charge compensation mechanism is provided by  $\text{H}^+$  vacancies in two opposite pairs of water molecules identified by Aleksandrov *et al* (1978) as molecule types I and II. This would lead to the existence of two different paramagnetic centres with similar values of the spin Hamiltonian parameters and different direction cosines. This is what is observed experimentally in the form of  $\beta$  and  $\beta'$  centres. In order to make a further step, one has to look at the EPR line intensities. The experiment shows that the line intensity observed for centre  $\beta$  is about ten times larger than that for centre  $\beta'$  suggesting that the probability of creation of centre  $\beta$  is about ten times larger than that corresponding to  $\beta'$ . Now, it is important to find out whether there exists any correlation between the principal directions measured experimentally and those set up by  $\text{O}(n)\text{--Cr}^{3+}\text{--O}(n')$  bonds. For a site of low symmetry one does not necessarily expect any clear correlation between the principal directions of  $\mathbf{D}$  and the  $\text{Cr}\text{--O}$  bond directions. However, examination of the ligand positions derived shows a curious and unexpected correlation, for both  $\beta$  and  $\beta'$  sites, between the direction cosines of the principal directions of the measured  $\mathbf{D}$  matrix and the directions of vectors joining the nuclei of ligands  $\text{O}(n)$  and  $\text{O}(n')$  on opposite sides of the  $\text{Cr}^{3+}$  ion. This correlation is shown in tables 4 and 5. Taking this and the molecular structure of the crystal into account, it may be concluded that for the  $\beta$  centre charge compensation is achieved by breakage of the 'curved' bonds in the water molecules related to  $\text{O}(5)$  and  $\text{O}(5')$  whereas for the  $\beta'$  centre charge compensation is achieved by breakage of bonds in the water molecules related to  $\text{O}(6)$  and  $\text{O}(6')$ . These two models of charge compensation are illustrated in figure 3.

In view of the apparent internal coherence of this SM analysis, it is of interest to examine more closely what actually happens to particular ligand positions during the phase transition. Therefore the calculations were repeated for two additional values of temperature, one just above the phase transition and one just below (see table 6). This analysis led us to the conclusion that between room temperature and 95 K the ligand bond lengths decrease with lowering temperature at a rate which can be easily explained by thermal contraction of the crystal. However, between 95 and 92 K the change is so large that it certainly cannot also be ascribed to thermal contraction; so it must be attributed to the effect of phase transition. Such a conclusion is clear from the temperature variation of the observed EPR spectrum (Kuriata *et al* 1995), but use of the SM gives a quantitative description of the phenomenon.

As mentioned in the preceding section, the calculated values of the spin Hamiltonian parameters  $b_n^m$  proved to be very sensitive even to small changes in angular positions of the oxygen ligands. Therefore, the observed splitting of all EPR lines for both  $\beta$  and  $\beta'$  centres after the phase transition, corresponding to the transition from  $P2_12_12_1$  to  $P2_1$  (see Kuriata *et al* 1995), could involve changes not only in metal–ligand distances but also changes in

angular positions of the ligands. However, the SM analysis shows clearly that within the whole temperature range the angular position of the ligands remained constant.

In conclusion, we comment that this paper constitutes only a sort of translation between spin Hamiltonian parameters measured experimentally for  $Cr^{3+}$  in SASD into geometrical parameters. It is probably too early to draw conclusions about the generality of the approach presented, but the method is worthy of more systematic study, preferably for less complex systems than SASD.

#### 4. Conclusion

It is shown that the application of the superposition model seems to be a valid tool for study of local distortions around  $Cr^{3+}$  ions, present as a dopant in low-symmetry systems such as SASD.

For the sites studied in this paper one obtains an internally consistent model explaining the relation between experimental EPR data and structural details including the model for charge compensation and the behaviour of the nearest neighbours during the phase transition.

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