

Studies of chromium-doped sodium ammonium sulphate dihydrate: I. Electron paramagnetic resonance of Cr^{3+}

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 2321

(<http://iopscience.iop.org/0953-8984/7/11/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 12:46

Please note that [terms and conditions apply](#).

Studies of chromium-doped sodium ammonium sulphate dihydrate: I. Electron paramagnetic resonance of Cr^{3+}

J M Baker†, J Kuriata‡, A C O'Connell† and L Sadlowski‡

† Oxford Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

‡ Instytut Fizyki, Politechnika Szczecińska, Alca Piastów 17, 70-310 Szczecin, Poland

Received 22 December 1994

Abstract. Electron paramagnetic resonance (EPR) of Cr^{3+} ions has been observed in single crystals of sodium ammonium sulphate dihydrate (SASD) doped with chromium. At 300 K the spectrum is relatively simple, exhibiting two main different sites, labelled α and β . The spin-Hamiltonian parameters for these sites have been measured. The relative concentration of different paramagnetic sites shows marked sensitivity to unknown factors in the crystal growth. On lowering the temperature the spectrum becomes very complex, making detailed study of the various sites, and changes at any phase transition, impossible to elucidate. None of the spectra shows a marked change at the ferroelectric transition temperature, $T_c = 92$ K.

1. Introduction

In order to understand the mechanisms of a phase transition in a solid, it is important to know the structural changes which occur at the transition. One technique which may be used to discover this information is EPR of either probe transition metal ions doped into the crystals, or paramagnetic radicals produced by irradiation, because the spectra of such species are sensitive to the nature and symmetry of their surroundings (Owens 1985).

In this paper, and the following one, we discuss the application of this technique to $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (which we refer to hereafter by the acronym SASD, sodium ammonium sulphate dihydrate), known in mineral form as lecontite, which becomes ferroelectric at 101 K, and has a further phase transition at 92 K (Pepinsky 1959, Makita and Sekido 1965). These papers are concerned with the EPR spectrum of Cr^{3+} . The EPR spectrum of radicals produced by x-irradiation in SASD has been discussed by Baker *et al.* (1993).

SASD, and the isomorphous material sodium ammonium selenate dihydrate (SASeD), are orthorhombic with space group $P2_12_12_1$ and four molecules in the unit cell in the paraelectric phase (Corazzo *et al.* 1967), and $P2_1$ in the ferroelectric phase (Aleksandrov *et al.* 1978). Figure 1 shows the structure of SASD, which may be regarded as chains of NaO_6 octahedra, sharing three O atoms on a face, approximately aligned along [001], interlaced with chains of $(\text{NH}_4^+)—(\text{SO}_4^{2-})—(\text{NH}_4^+)$, the two types of chain being linked by sharing one O in the SO_4 tetrahedra and hydrogen bonds. Chains containing Na are quite separate; they do not share the same SO_4 tetrahedra. The materials are of interest because they contain NH_4 and H_2O , both of which have been found to be active in the ferroelectric transition in similar materials (Genin and O'Reilly 1969).

However, Genin and O'Reilly have shown using proton and deuteron NMR in SASD that the P–P and D–D directions for the water molecules do not change at either of the transition

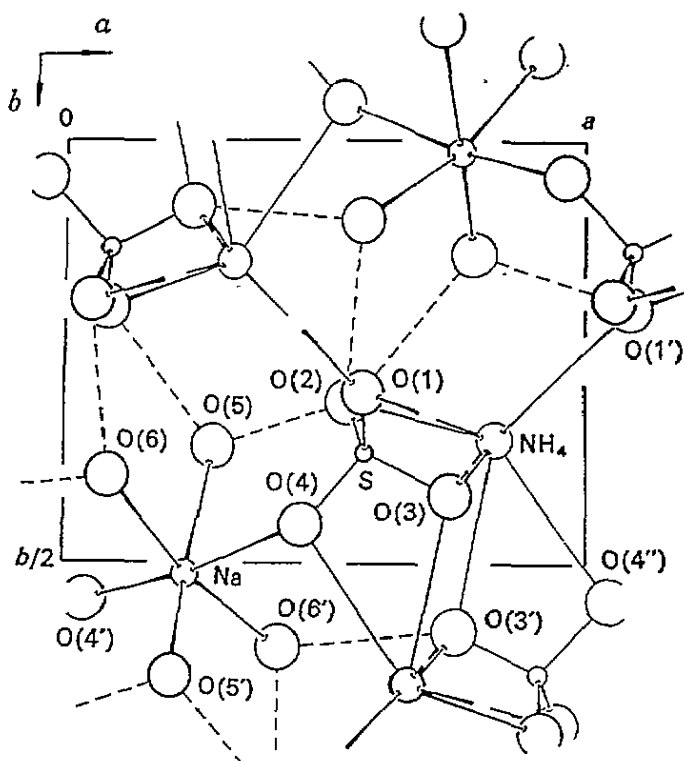


Figure 1. The crystal structure of SASD viewed along [001].

temperatures, suggesting that the water molecules are not involved with the ferroelectricity. Further, lack of change in the deuteron NMR of ND_4^+ shows that the radical does not undergo distortion at either of the transitions; and the quadrupole interaction shows that ND_4 is a perfect tetrahedron. However, at 111 K, there is a change in the activation energy for rotation about the threefold axis of NH_4 , as detected by proton relaxation rates; and also a marked separation into two types of Na site as shown by a splitting of the quadrupole satellites of the ^{23}Na NMR for external field parallel to [100]. This indicates that there are lattice displacements at 101 K, though there are no similar effects at 92 K. The four Na sites, equivalent under $P2_12_12_1$ split into two pairs equivalent under $P2_1$ for $T < T_c$. The absence of involvement of motion of NH_4 in the ferroelectricity is confirmed by the lack of a large change in T_c on deuteration of the material.

It is suggested by Ramani and Srinivasan (1981) that at room temperature the rapid reorientation of NH_4 and SO_4 radicals results in a structure dominated by ionic bonding. Both motions slow down as T is reduced, so allowing hydrogen bonding to play a more prominent role, with consequent atomic displacements. NH_4 is supposed to slow first as T is reduced, leaving the slowing of SO_4 to determine T_c : ionic displacements in the sodium-oxygen octahedra and consequent displacements in the tetrahedral groups are supposed to lead to the ferroelectricity.

EPR has been studied by Ramani and Srinivasan (1981) in SASeD , where the ferroelectric transition temperature is 180 K. Irradiation with ^{60}Co γ -rays produced the radicals SeO_4^- , SeO_3^- and SeO_2^- , identified from their \mathbf{g} -matrices and the ^{77}Se hyperfine matrices. The involvement of SeO_4^- in the ferroelectric transition is shown by the change of \mathbf{g} -matrix for

SeO_4^- from isotropic at room temperature to rhombic close to T_c . This contrasts with the \mathbf{g} -matrices of SeO_3^- and SeO_2^- , which show no change at T_c .

EPR has been measured by Lakshmana Rao *et al* (1990) in SASD doped with Cu^{2+} between 300 and 77 K. One set of symmetry-related sites was observed with axially symmetric \mathbf{g} - and \mathbf{A} -matrices, the latter inferred from line width caused by unresolved Cu hyperfine structure. \mathbf{g} and \mathbf{A} are temperature dependent, but show no abrupt change at T_c . It is postulated that Cu^{2+} occupies a Na^+ site.

2. Experimental details

EPR was measured in standard spectrometers at two microwave frequencies near 9.4 and 35 GHz both using 115 kHz modulation of the applied magnetic field and subsequent phase sensitive detection. The applied magnetic field \mathbf{B} could be rotated about a vertical axis to investigate the angular dependence of EPR in a horizontal plane in the sample. The microwave cavity containing the sample could be operated either at room temperature, in a bath or refrigerant at 77 K or 4 K, or in a Oxford Instruments CF200 helium-gas-flow cryostat for continuous variation of temperature from 4 to 300 K. However, the precise temperature of the sample was not known because the temperature of the gas had to be sensed outside the resonance cavity.

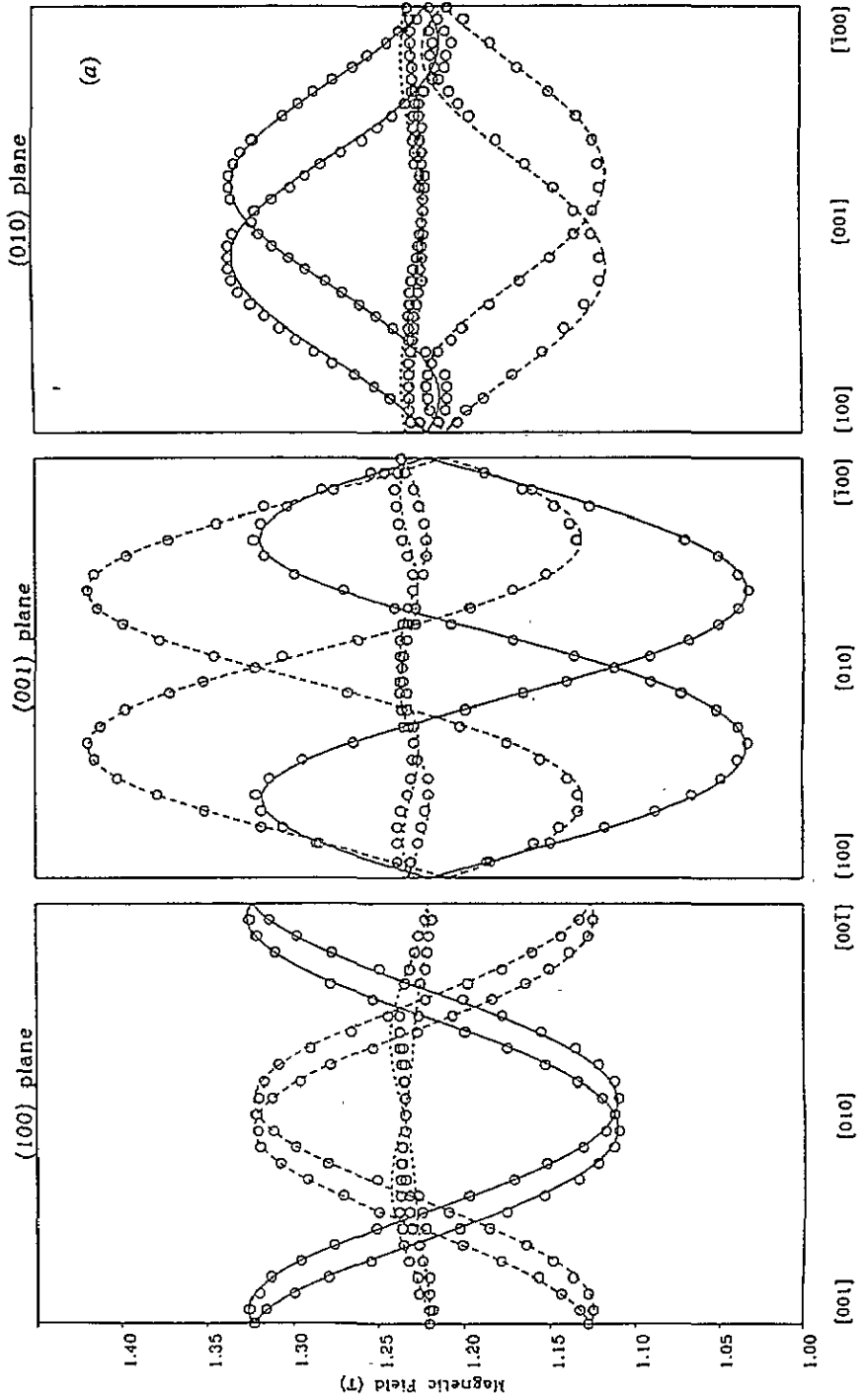
Large, good quality, single crystals of chromium-doped SASD were grown from a saturated aqueous solution of equimolar ratio $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 , to which the chromium was added in the form of $\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, by slow evaporation, as the temperature was decreased at 0.4 K per day from 304 to 299 K.

Crystals of SASD from aqueous solution have well formed faces. In spite of the lattice parameters having ratios close to those of simple numbers, there was no evidence of twinning of the crystals. The symmetry axes are easily recognised from the morphology of the crystals. Well formed (100), (010) and (001) faces made it easy to cut specimens in the form of approximately 2 mm cubes with faces oriented to better than 1° , and facilitated the mounting of the crystals, allowing measurement in these symmetry planes. Any slight misorientation of the plane could be compensated by tilting the cryostat through a small angle.

As the EPR spectra measured showed no site symmetry, each site gives rise to four spectra related by the symmetry operations of the crystal. Most measurements were therefore made in the planes of reflection symmetry where sites are equivalent in pairs; and the simplest spectra occur when the external field is along one of the crystal axes, when all four sites are equivalent.

3. The EPR spectrum

Samples doped with chromium yielded a well resolved spectrum with about 25 lines varying in intensity and width over a range 0.6 to 1.7 T at 35 GHz. Their angular variation was measured in the (100), (010) and (001) planes. Figure 2 shows this for two sets of strong narrow lines (2 mT) belonging to two different sites, labelled α and β . There were also several much weaker lines (about 2% of the intensity of the strong lines) and also several broader lines (8 mT). The relative intensities of sites α and β varied from crystal to crystal. The site symmetry, and consequent line degeneracy in the {100} planes, does not allow from measurement only in these planes an unambiguous assignment of the angular variation of any particular site (or a determination of the relative signs of the spin-Hamiltonian parameters),



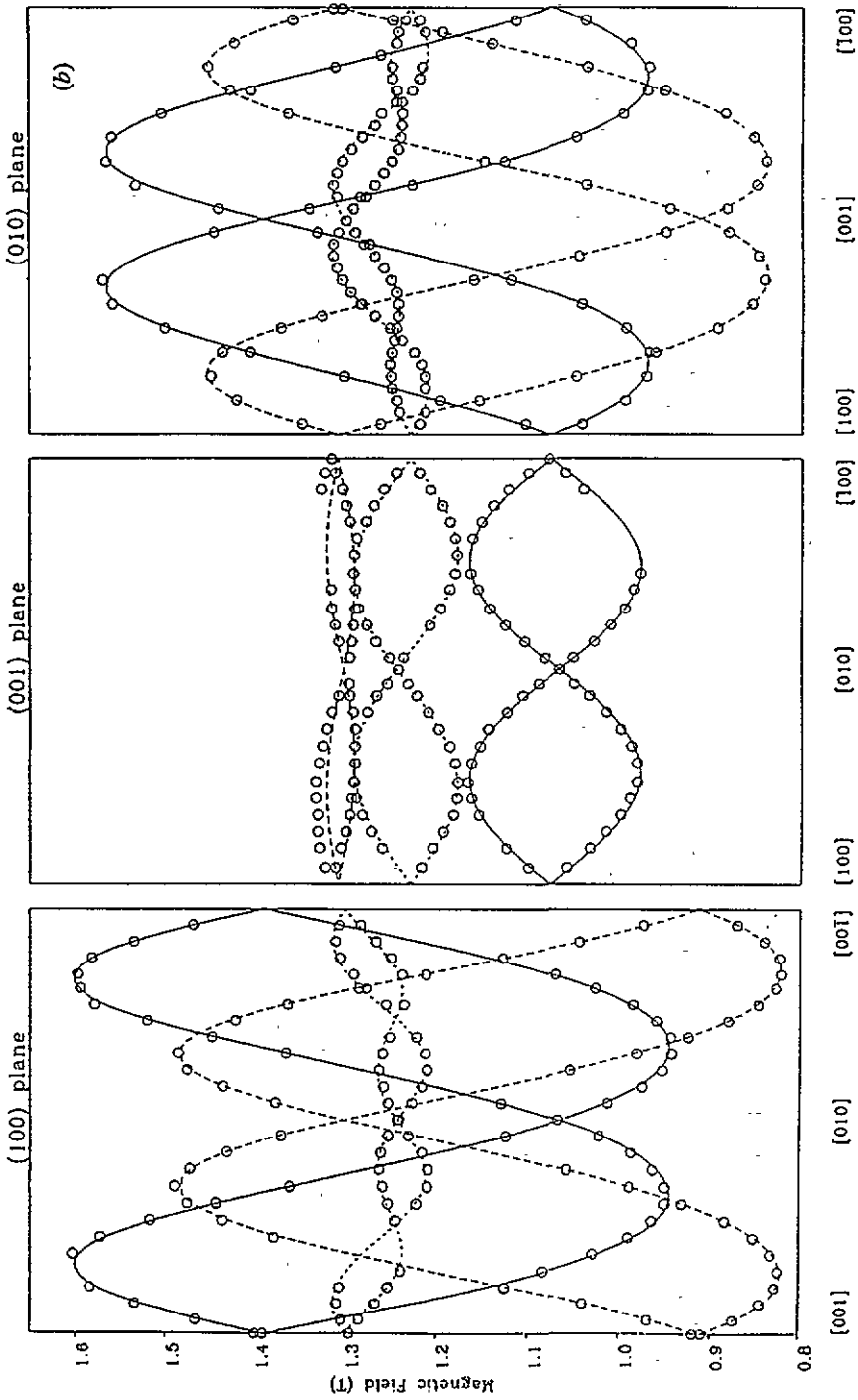


Figure 2. Angular variation of the EPR spectra of (a) α - and (b) β -sites in chromium-doped SASD at 300 K and near 35 GHz. The smooth curves indicate the angular variation computed using the parameters for best fit. The dashed curves in the centre of each spectrum are the $1/2 \leftrightarrow 1/2$ transitions; the curves for the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions are distinguished, one being dashed and the other continuous.

so it was necessary to make one measurement in a plane close to $\{111\}$.

As the α - and β -spectra appeared each to comprise three lines from four symmetry-related sites, and Cr^{3+} was an expected impurity in the crystals, these spectra were fitted to the spin Hamiltonian with $S = 3/2$

$$\mathcal{H} = \mu B \cdot \mathbf{g} \cdot \mathbf{S} + S \cdot \mathbf{D} \cdot \mathbf{S} \quad (1)$$

Perturbation theory was adequate to find starting parameters, and the parameters listed in table 1 were obtained by a least-squares optimization to the diagonalization of the full spin Hamiltonian. Interdependence of the parameters makes error analysis difficult, so a Monte Carlo method of averaging the results of several repeated convergences, each acting on a different data set $\{x(i)(1 + \delta), y(i)(1 + \delta)\}$, where δ is a random Gaussian error estimate, was used to give an indication of the errors on each predicted parameter. This method reconstructs extremely well the high-field transitions for the β -site in the (001) plane, which was not included in the fitting as we had only poor data.

Table 1. Spin-Hamiltonian parameters for α - and β -sites in chromium-doped sAsD. Only relative signs of the principal values have been determined. Direction cosines (l , m , n) are relative to crystallographic axes [100], [010] and [001].

Site	g -value	Principal value of D (MHz)	l	m	n
α	1.981(4)	-1779(8)	-0.557(8)	-0.606(2)	0.568(4)
		529(8)	0.831(4)	-0.407(6)	0.380(2)
		1249(6)	0.001(2)	0.683(6)	0.730(2)
β	1.987(8)	-3625(10)	0.582(6)	0.743(9)	0.332(7)
		-602(7)	0.635(8)	-0.670(4)	0.386(6)
		4228(10)	-0.509(4)	0.014(4)	0.861(3)

As only α -spectra were observed from one batch of crystals, and in the other the α -site is much stronger than the β -site, we presumed that the α -site corresponded to Cr^{3+} , but we examined the possibility that the β -site was Fe^{3+} in which we were failing to observe the $|\pm 5/2\rangle \leftrightarrow |\pm 3/2\rangle$ transitions. This would be quite possible for the weak β -spectrum where there was evidence of a mosaic spread of D -values from the width of the $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ transitions. An attempt to fit spin Hamiltonian (1) with $S = 5/2$ to our data produced spin-Hamiltonian parameters for which the reconstructed angular dependence contained peculiar 'humps' in the otherwise smooth angular variation, quite different from that observed, which arise because the derived parameters produce large admixtures between states. The humps are too large to be removed by fourth-order terms in the spin Hamiltonian of the order of those which have usually been observed for Fe^{3+} . Hence we conclude that the β -site is a second Cr^{3+} site. This identification is confirmed by a reconstruction of 'forbidden' $\Delta M_S = \pm 2$ transitions, which fit very well with the angular variation of some of the weaker lines at low fields.

4. Temperature dependence of the EPR spectrum

The temperature variation of the spectrum is very striking, as shown in figure 3. The sample used for this investigation had very small concentration at the β -site, so the room temperature spectrum is primarily the α -site. As T is lowered the α -lines tend to become weaker, and split slightly at T_c , but only by 20 mT for [001]. Many other lines appear in the spectrum, gradually increasing in intensity (some because they gradually decrease in width)

as T decreases, some of them growing from zero intensity at room temperature to dominate the spectrum at low temperatures. Many lines show gradual changes in position, as one might expect from the effect of thermal contraction on zero-field splittings of S -state ions. They show no marked change at T_c . The spectrum well below T_c becomes so complex that it is difficult to know whether there are abrupt changes indicating further transitions. The complexity at low temperatures makes it possible to follow the angular variation of only a few lines in the whole spectrum, which appears to arise from many species of S -state ion, so that useful measurement can be made only for B along crystal axes.

Only the α -site shows any obvious change at T_c , and that only in the [001] direction; there appears to be no line splitting in [010], and for [100] the α -spectrum is too confused by superposition on other spectra for any splitting to be observable. The [001] direction shows the splitting into two which one would expect at the ferroelectric phase transition, though by only the very small value of 20 mT, which corresponds to a change in D_{zz} of $\pm 5\%$; but unexpected and unexplained is the fact that on further cooling, one of the lines becomes very weak and eventually disappears: it is as if one sublattice is becoming overwhelmingly populated at the expense of the other. It is possible to follow the angular dependence of the α -lines in the (010) plane, where they follow much the same path as at room temperature, confirming that the changes in D are not large.

5. Discussion of atomic models of Cr^{3+}

It is likely that Cr^{3+} would be incorporated in the SASD lattice at either a Na^+ or a NH_4^+ site, providing a superficial explanation of the occurrence of two different sites. Cr^{3+} is considerably smaller than either Na^+ or NH_4^+ , so one might expect considerable local distortion, as well as some sort of charge compensation. As the Na^+ site, in an irregular octahedral array of six O^{2-} ligands, seemed a more likely site for Cr^{3+} , we examined the possibility that this was the α -site.

Table 2. Ligand bond directions derived from the crystal structure of SASD (Corazzo *et al* 1967). Direction cosines (l , m , n) are relative to crystallographic axes [100], [010] and [001]. To generate direction cosines for the other three symmetry-related sites, the signs in any two of the columns l , m , n should be reversed.

Bond	Bond length (nm)	l	m	n
Na-O(6)	0.247	-0.518	-0.579	0.632
Na-O(5)	0.240	0.183	-0.804	-0.567
Na-O(4)	0.245	0.759	-0.314	0.571
Na-O(6')	0.242	0.632	0.430	-0.645
Na-O(5')	0.235	-0.081	0.655	0.749
Na-O(4')	0.238	-0.676	0.164	-0.718
Na-Na'	0.315	0.079	-0.124	0.990
Na-Na''	0.315	0.079	-0.124	-0.990

It is not clear which of the four observed D -matrices should be assigned to each of the four Na^+ sites. Table 2 lists the ligand bond directions for one of these sites, calculated from the crystal structure of Corazzo *et al* (1967), and explains how to generate those for the other three sites. There is no obvious relationship between any of these sites and the principal direction of the D -matrix. As this may be due to the very low symmetry of the site, we attempted a calculation of the D -matrix set up by the six O^{2-} ligands using the superposition model of Newman (Bradbury and Newman 1967, Newman and Ng 1989).

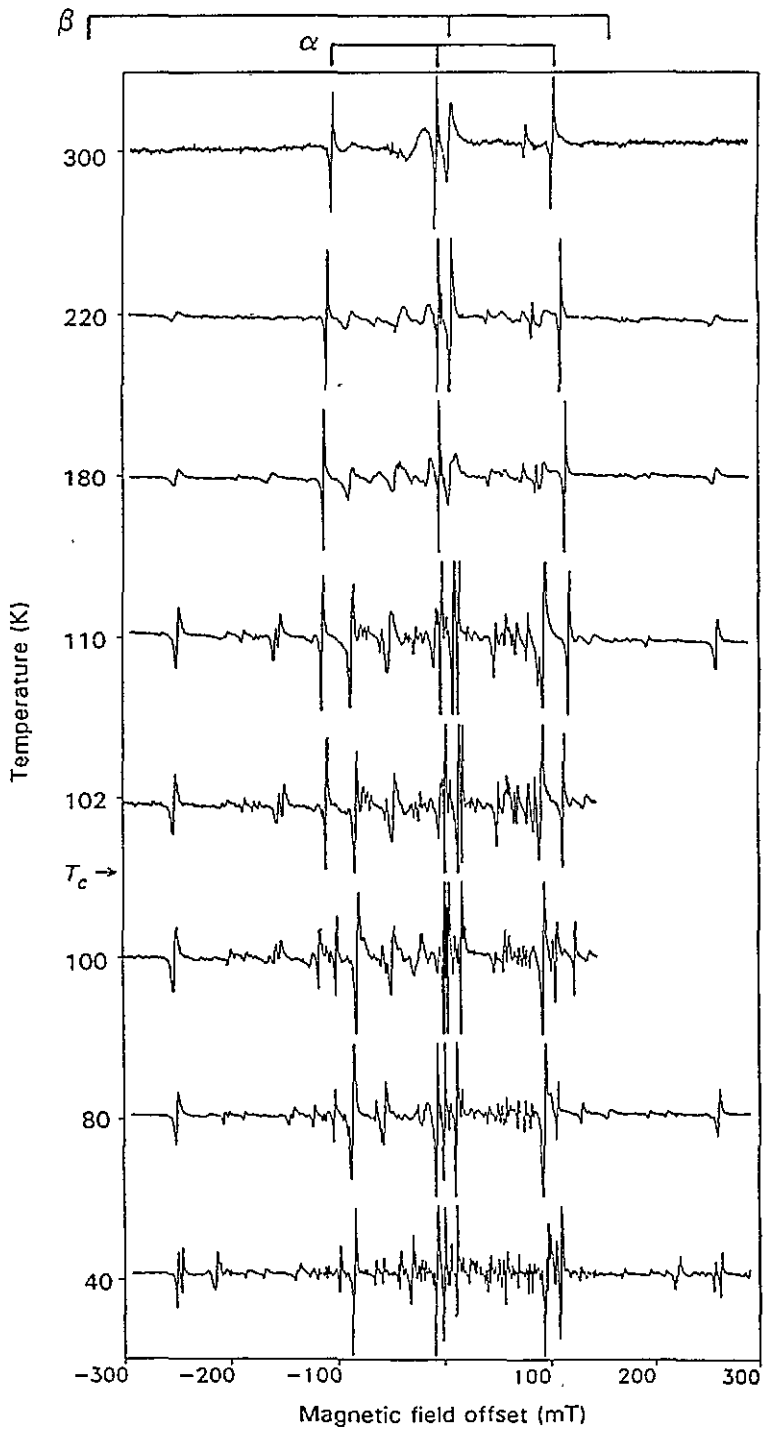


Figure 3. Temperature variation of the EPR spectrum of chromium-doped SASD for B parallel to $[001]$.

Muller and Berlinger (1983) has applied this model to Cr^{3+} in a number of oxides. In this model, the contribution from each ligand is assumed to be axially symmetrical about the bond direction, and to be independent of the identity of the host lattice, depending only upon the type of ligand and its distance R . The second-order intrinsic parameter is given by

$$b_2(R) = -A(R_0/R)^{10} + B(R_0/R)^{13} \quad (2)$$

and the second-order contribution to the spin Hamiltonian has the form

$$\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} = \sum_m b_2^m O_2^m(S) = \sum_m \sum_i K_2^m(\theta_i \phi_i) b_2(R_i) O_2^m(S) \quad (3)$$

where $O_2^m(S)$ are second-order Stevens operators (Stevens 1952), and the values of $K_2^m(\theta \phi)$ are tabulated by Newman and Ng (1989). The coefficients of the \mathbf{D} -matrix are then given by

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

Muller and Berlinger (1983) list parameters A , B and R_0 for Cr^{3+} at sites of metals ions (Me^{n+}) of varying valency from Me^{4+} (SrTiO_3) to Me^{2+} (MgO). We have extrapolated parameters for Me^+ (Na^+) giving for $R_0 = 0.219$ nm, $A = -7.3$ cm^{-1} and $B = -5.3$ cm^{-1} . Figure 3 shows the R -dependence of b_2 , including our extrapolated curve for Me^+ . Using these parameters with the lattice coordinates of O from the crystal structure data gives the \mathbf{D} -matrix in table 3.

Table 3. Parameters of the \mathbf{D} -matrix calculated for Cr^{3+} at the Na^+ site in SASD using the superposition model. Direction cosines (l , m , n) are relative to crystallographic axes [100], [010] and [001].

Principal value D_i/h (MHz)	l	m	n
-82850	-0.40	0.91	0.09
-12750	0.68	0.36	-0.64
95600	0.62	0.19	0.76

Two things are clear from this. The first is 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 such low symmetry. Secondly, the calculated parameters are an order of magnitude larger than those we measure for the α -site.

This indicates that the sites we are observing are not Cr^{3+} at undistorted Na^+ sites. The distortion may be estimated using ionic radii from Kaminskii (1975)—for sixfold coordination: 0.062 nm for Cr^{3+} and 0.102 nm for Na^+ ; and 0.135 nm for twofold coordinated O^{2-} . Both that Cr^{3+} is a smaller ion than Na^+ , and that its charge is larger, would tend to decrease the ligand bond lengths in the Cr^{3+} -substituted site. Figure 4 shows that if R were reduced to 0.197 nm, the sum of the ionic radii of octahedrally coordinated Cr^{3+} and O^{2-} , b_2 would become very small, and even of uncertain sign, making it possible to reduce the predicted D -parameters.

If Cr^{3+} substitutes for Na^+ , charge compensation could be achieved by positive-ion vacancies, or by proton vacancies causing ligand water molecules to become OH^- or O^{2-} . As the loss of protons would not greatly change the crystal field set up by O^{2-} it seems

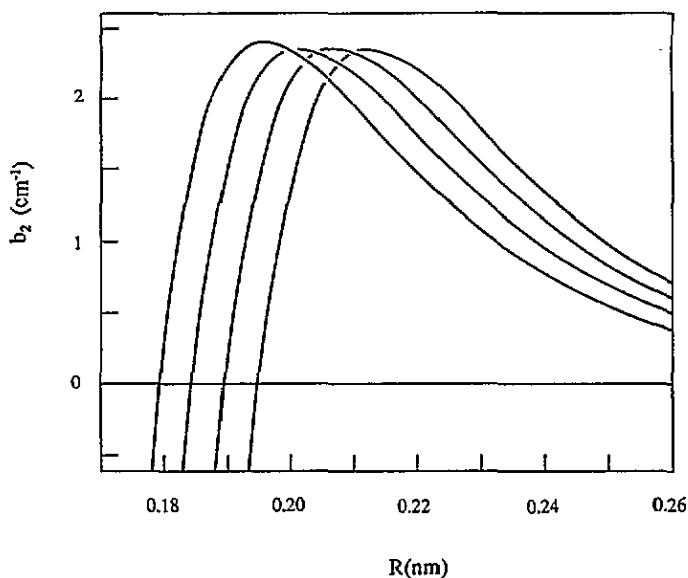


Figure 4. The dependence of the intrinsic parameter b_2 upon ligand distance R , for Cr^{3+} replacing Me^{n+} ; from right to left, the curves are for $n = 1, 2, 3, 4$.

unlikely that this is the mechanism of charge compensation needed to produce a smaller crystal field.

If compensation is achieved by two close Na^+ vacancies, at sites on either side of Cr^{3+} in the same chain, it would break the linkage in the chain, and leave CrO_6 , or more correctly $[\text{Cr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]^-$, floating fairly free and loosely attached to the NH_4 chain. One might then expect the freed oxygens to shrink onto Cr^{3+} to form a more regular octahedron with smaller Cr–O bond lengths. This could correspond to the α -site.

If the β -site were Cr^{3+} at a NH_4^+ site, one might expect, as the $(\text{NH}_4)\text{--O}$ distances are very much larger than the sum of the ionic radii of Cr^{3+} and O^{2-} , that Cr^{3+} would move towards one of the SO_4 tetrahedra leading to a strong axial D -matrix, much larger than that observed.

The β -site could correspond to Cr^{3+} in a Na^+ site with one Na^+ vacancy, the other charge-compensating site being remote, or a single OH^- . Even though Cr^{3+} would still be attached to the NaO_6 chain on one side, it could still distort to shorten the Cr–O bonds, but now probably with a bias towards the Cr–Na direction. The shorter bonds would decrease b_2 , but the constraint of attachment to the chain might cause larger angular distortion from orthorhombic bond directions, so leading to somewhat larger D -parameters, as observed. However, for Cr^{3+} at any site, there are two possible sites for the adjacent Na^+ vacancy, which are not equivalent and not related by any symmetry operation; so one might expect two different sites. If the second charge were compensated by OH^- , this might be expected to produce four different sites for each site of the Na^+ vacancy, unless there was tunnelling of the H^+ vacancy between the four water molecules.

There are two reasons for it seeming unlikely that we have Cr^{3+} substituted for Na^+ compensated by NH_4^+ vacancies: (a) it would leave Cr^{3+} in an almost undistorted Na^+ site, for which we have shown that D -parameters would be much larger than observed; (b) there are several different NH_4^+ sites, so any distortion produced by the vacancy would lead to a multiplicity of Cr^{3+} sites with similar but slightly different D -parameters, which is not

observed.

The very small change in the α -site at T_c supports the suggestion that this site is somewhat detached from the rest of the lattice, and so does not participate in the full structural distortion at T_c . The apparently much smaller changes in any of the other sites at T_c suggests that they are even less strongly coupled to the lattice. The gradual appearance of more and more sites, presumably for Cr^{3+} , may be related to association with NH_4 tetrahedra which are in motion at room temperature and so smearing out the fine structure, but become frozen in at low temperatures; the great multiplicity of sites may be related to different types of NH_4^+ vacancy. It is also possible that some of these sites are associated with OH^- compensation, for which at room temperature tunnelling of the proton vacancy may broaden the EPR, but may become quenched into one of the many sites at lower temperatures. It is possible that some of the new sites arise from Fe^{3+} —though it is not clear why, if there is appreciable Fe^{3+} in the crystal, some of it is not incorporated into sites which are observable at room temperature.

6. Conclusions

We have found, unlike in most other similar systems, very complicated EPR spectra at low temperatures in chromium-doped crystals of SASD. None of these spectra shows a marked change at T_c . This has been taken to indicate that all of the paramagnetic species observed are somewhat detached from the lattice in which they are embedded. The complexity of the EPR spectrum, combined with the very small changes in the spectrum, makes it impossible to extract information about structural changes at T_c with any certainty. Another noticeable feature of SASD is a marked sensitivity of the relative concentrations of the different paramagnetic species to unknown factors in the crystal growth.

References

- Aleksandrov K S, Alexandrova I P, Shabanov V F, Yuzvak V I, Nozik Y Z and Fikin L I 1978 *Phys. Status Solidi* a 45 53
- Baker J M, Cook M I, Tronconi A L, Kuriata J and Sadlowski L 1993 *J. Phys.: Condens. Matter* 5 459
- Bradbury M I and Newman D J 1967 *Chem. Phys. Lett.* 1 44
- Corazzo E, Sabelli C and Guiseppetti G 1967 *Acta Crystallogr.* 22 683
- Genin D J and O'Reilly D E 1969 *J. Chem. Phys.* 50 2842
- Kaminskii A A 1975 *Laser Crystals* (Moscow: Nauka) p 256
- Lakshmana Rao J, Murali Krishna R, Lakshman S V J and Chand P 1990 *J. Phys. Chem. Solids* 51 323
- Makita Y and Sekido T 1965 *J. Phys. Soc. Japan* 20 954
- Muller K A and Berlinger W 1983 *J. Phys. C: Solid State. Phys.* 16 6861
- Newman D J and Ng B 1989 *Rep. Prog. Phys.* 52 699
- Owens F J 1985 *Phase Transitions* 5 81
- Pepinsky R 1959 *Lectures on Ferroelectricity* (Moscow: Institute for Crystallography, Academy of Sciences, URRS)
- Ramani K and Srinivasan R 1981 *Mol. Phys.* 44 125
- Stevens K W H 1952 *Proc. Phys. Soc. A* 65 209