Studies of chromium-doped sodium ammonium sulphate dihydrate: II. Electron paramagnetic resonance and dielectric susceptibility measurements of chromium-rich regions

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Abstract. Some crystals of chromium-doped sodium ammonium sulphate dihydrate (SASD) appear to be divided into regions of darker and regions of lighter blue coloration. Crystal specimens cut from the darker regions have been investigated. Their EPR spectrum exhibits, in addition to the β-site previously measured, a new site, labelled β' because of its similarity to the β-site. The spin-Hamiltonian parameters of the β'-site have been measured at 300 K, and the temperature dependence of the spin-Hamiltonian parameter D has been measured from 300 K to 77 K. In contrast to the α-site described previously, the β'-site shows a marked doubling below 92 K, corresponding to a change in D.

The temperature dependence of the dielectric susceptibility shows a marked change at 204 K, only very slightly noticeable in undoped SASD, which correlates with a change of slope in the temperature dependence of D measured by EPR.

1. Introduction

Some crystals of sodium ammonium sulphate dihydrate (SASD), grown presumably under somewhat different conditions from those described in the previous paper (Baker *et al* (1995), hereafter labelled I), were found to contain regions of much stronger blue coloration, indicating higher Cr^{3+} concentration. The crystals grew as rectangular plates parallel to the (001) plane, and these were divided by a diagonal cross into dark and light regions. This suggests that the take up of Cr^{3+} is faster on some growth planes than on others. Optical absorption spectra taken for light and dark regions of the crystal indicate that the concentration of Cr^{3+} in dark regions is about three times higher than that in light ones (see figure 1). The morphology of the dark regions was also obviously different from that of undoped crystals of SASD.

2. EPR measurements

Specimens cut from these more strongly coloured regions gave EPR spectra with a very low concentration of the α-sites described in I; and, in addition to the β-site, they gave a strong spectrum from another previously unobserved site, labelled β', whose principal values of the **D**-matrix are similar to those of the β-site, but with different principal directions. The
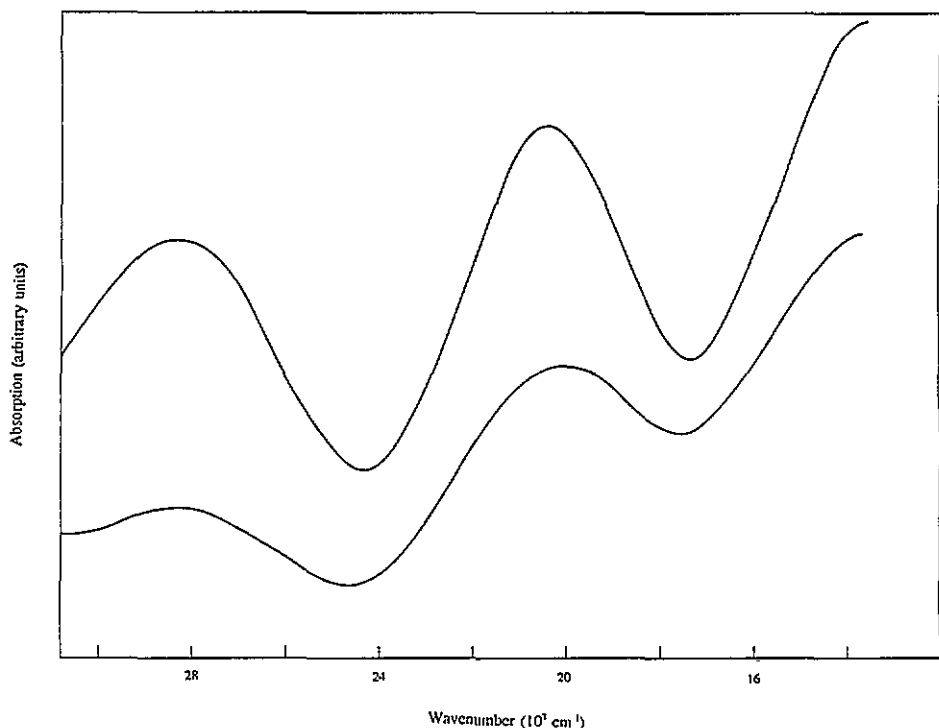
Figure 1. Optical absorption spectra for light and dark regions of $NaNH_4SO_4 \cdot 2H_2O{:}Cr^{3+}$.

intensities of β- and β'-sites were similar. The angular dependence of the EPR spectrum was measured at room temperature in the principal crystallographic planes (100), (010) and (001).

Analysing the spin Hamiltonian for $S = 3/2$ in the form

$$H = g\mu_B B \cdot S + S \cdot D \cdot S = g\mu_B B \cdot S + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \qquad (1)$$

we obtained the parameters listed in table 1.

Table 1. Spin-Hamiltonian parameters for the β'-site in chromium-doped SASD. Direction cosines (l, m, n) are relative to crystallographic axes [100], [010] and [001].

g-value	Principal value of D (MHz)	l	m	n
1.98(1)	$-1003(15)$	0.514(37)	$-0.548(34)$	0.659(32)
	$-2829(20)$	0.681(31)	$-0.218(42)$	$-0.700(36)$
	3832(15)	0.522(37)	0.808(25)	0.275(42)

The magnetic field B was also aligned along the principal direction of D corresponding to the maximum separation of the $\pm 3/2$ to $\pm 1/2$ transitions by rotation of the crystal about one axis and the magnetic field about an orthogonal axis. From this maximum separation the principal value D_{zz}, and hence the value of D, is confirmed accurately, and the value of E is measured with relatively low accuracy from second-order effects, for B aligned along this one direction.

The close similarity of the principal values for the β- and β'-sites made it important to establish that they were not the same site in a twinned crystal. That they are different sites is

demonstrated by: (a) the method of finding turning points for extremal separation of spectral lines giving different results for the two sites well outside the precision of measurement; and (b) although this method gives much lower precision for principal directions, those for the two sites differ by more than the precision of measurement. Hence it is clear that there are two closely similar sites, and it is worth noting that one is almost generated from the other by a permutation of crystal axes

The EPR spectra are very complex, with many forbidden lines, so studying the temperature dependence of the angular variation of the spectrum would have been very difficult, as it was for the spectra described in I. However, by orienting B along the principal direction corresponding to D_{zz}, as described above, it was possible to obtain spectral lines in extremal positions for the β'-site which were well separated from the rest of the spectrum. The temperature dependence of these lines could be followed without confusion by the rest of the spectrum. However, as the measurements were made only along the principal direction, it was possible to obtain accurate parameters only for D_{zz}, together with less precise values of E. The field B was set along the principal direction at room temperature, and remained along that direction for the measurement of temperature dependence. Although it was not confirmed at each temperature whether this direction remained a principal axis, it was confirmed that below 95 K this axis remained unchanged. The temperature variation of D_{zz} is shown in figure 2. There are two regions of approximately linear variation, due presumably to thermal expansion and coupling of the ion to the lattice vibrations (Owens 1979).
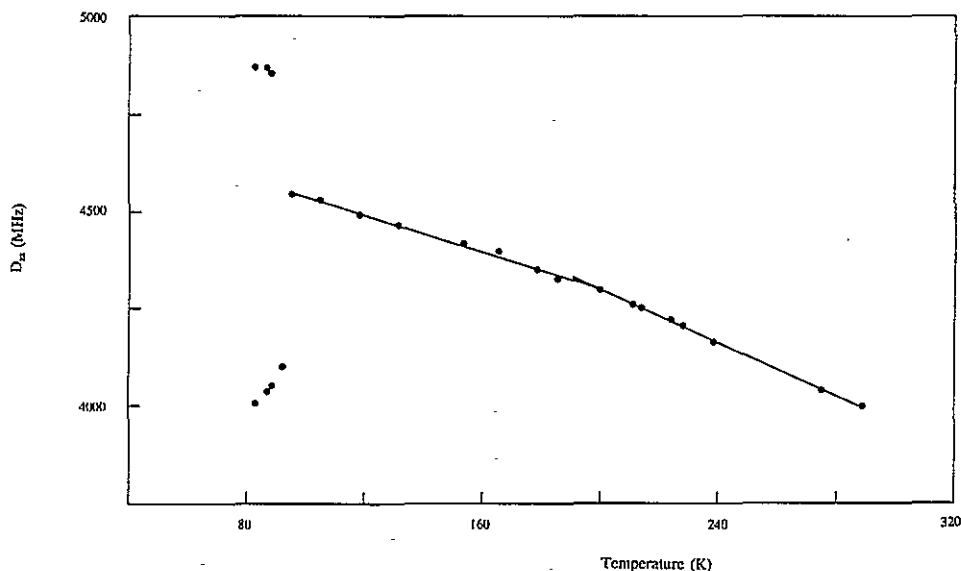

Figure 2. Temperature dependence of D_{zz} for the β'-site.

The phase transition at 95(±0.5) K is marked by a large doubling of the spectral lines, caused by the doubling of the unit cell of the crystal in the transition from the paraelectric phase with space group $P2_12_12_1$ to the ferroelectric one with space group $P2_1$. Below the transition, the temperature dependence of D becomes non-linear in agreement with the discussion by Owens (1979) for a complex with no centre of inversion.

Also, there is a change in slope of $D(T)$ at 195±5 K. The much less precisely determined temperature dependence in the value of E also appears to show a marked change of slope

at the same temperature, though it was difficult to establish whether there was any change at 95 K.

3. Dielectric susceptibility measurements

The dielectric susceptibility measurements were made at 20 kHz using a Hewlett-Packard bridge, type 4284 A, by plating silver electrodes onto the planes perpendicular to the principal direction for the β-site for a piece of a crystal cut from the dark blue region, and some control measurements were made for pure samples by plating electrodes on to the (001) planes of a parallel-sided specimen. The temperature dependence of the dielectric susceptibility for a piece of a crystal cut from the dark blue region is shown in figure 3. The low-temperature part of this is similar to that previously measured (see, e.g., Makita and Sekido 1965, Osaka 1978) for undoped SASD, showing a marked change at the phase transition measured by us at 101 ± 1 K.
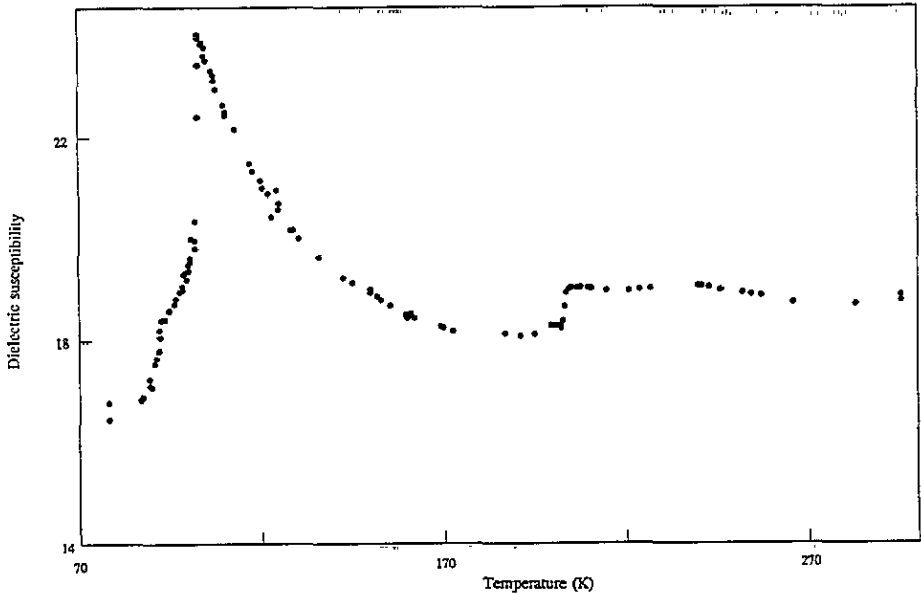

Figure 3. Temperature dependence of the dielectric susceptibility for a chromium-rich sample.

There is also a small change of 4.1% at 204 ± 1 K, the similar temperature at which the slope of the dependence of D_{zz} upon T changed. As far as we know, the existence of this anomaly has not yet been reported in the literature and we were inclined to assume that it reflects a transition caused by the large Cr^{3+} content in the crystal. However, a closer examination of the dielectric susceptibility measured at around 200 K for undoped samples, and a possibly accidental deviation of one point at the same temperature in the temperature dependence of the second moment of the NMR proton line for SASD shown in figure 1 in the paper of Makita *et al* (1967), suggests that there may be a slight anomaly at about 200 K. This fact undermines our first supposition and now we can only claim that the large content of Cr^{3+} in SASD makes the transition at about 200 K more noticeable by both EPR and dielectric susceptibility measurements.

The microscopic nature of the phase transitions occurring in SASD needs separate and more elaborate studies.

4. Conclusions

(i) Although many previously studied paramagnetic centres in SASD are very insensitive to the changes connected with phase transitions, the centres described in this paper seem to be coupled to the lattice strongly enough to follow clearly these phase transitions using EPR.

(ii) Both EPR and dielectric susceptibility measurements suggest that at about 200 K the crystal undergoes yet another phase transition not described so far in the literature.

(iii) The EPR data showed that the properties of crystals are extremely sensitive to unknown growth conditions, which through all our studies on SASD were believed to be the same.

Acknowledgments

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