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The ESR spectra of NSO_4^{2-} in $(\text{NH}_4)_2\text{SO}_4$

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The slow decay of NH_3^+ and NH_2^+ centers in ammonium sulfate produce a new, very stable, paramagnetic center that has been identified as NSO_4^{2-} . This center has g values of $g_x = 2.012$, $g_y = 2.011$, and $g_z = 2.007$ with the corresponding hfi constants $A_x = A_y = 0.0$ and $A_z = 25.2$ G. No change in this center is observed on passage of the crystal through the ferroelectric phase transition.

I. INTRODUCTION

X irradiation of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ at room temperature (RT) produces several different paramagnetic centers. Two of these NH_3^+ and SO_3^- have been reported on.¹ In addition, heating an $(\text{NH}_4)_2\text{SO}_4$ crystal to near its decomposition temperature (280 °C) produces a triplet state center that has been identified as NH_2^+ .² Although all of these centers are quite stable (no noticeable change in a week or so) after six months, these centers are no longer present in the crystal and a new center appears that is apparently the decay product of most of these centers. We report on this new center here. A preliminary report on this work has been presented.³

Ammonium sulfate is a ferroelectric crystal with a phase transition at -50 °C.⁴⁻⁶ A three dimensional neutron-diffraction study by Schlemper and Hamiltonian showed that the crystal is orthorhombic with a space group $Pnam$ at RT.⁷ The three twofold-rotation axes a , b , and c give unit cell dimensions of 7.782, 10.636, and 5.993 Å, respectively. This means that there is an ab mirror plane and also a center of inversion symmetry. Furthermore, the eight ammonium ions in a unit cell are of two different types (inequivalent). The two types have slightly different local environments. Because of inversion symmetry each of these two types, consisting of four ions each, as well as the four sulfate ions in the unit cell, will separate into at most pairs of equivalent (except for orientation) sites as far as ESR studies are concerned.

II. EXPERIMENTAL PROCEDURE

Single crystals were grown by slow evaporation from solution using reagent grade chemicals. The ESR studies reported here were made on crystals 6 months to a year after paramagnetic centers had been produced either by x rays or the heating of the crystal to near its decomposition temperature.^{1,2}

ESR measurements were made at X band (9 GHz) with a Jeolco JES-ME-IX spectrometer which has been modified to work with a Varian 12 in. magnet with a "Fielddial" magnetic field sweep. The klystron frequency was measured with a Hewlett Packard X532B frequency meter while the magnetic field was calibrated using a Magnion NMR gaussmeter. Measurements between liquid nitrogen and RT were made using a Jeolco variable temperature controller.

III. RESULTS AND THEORY

A three line spectrum with maximum splitting when H is parallel to the c axis is observed. This splitting collapses to a single line where H is parallel to either the a or b crystal axis. With a general orientation of H in the ab mirror plane that single line splits into two lines indicating two different orientations of the center.

Thus, the spectrum can be explained by an electron interacting with a single nucleus of spin 1 but having two different orientations in the crystal. We make the assumption that the hfi tensor and the g -value tensor have the same axes. Using the Hamiltonian derived previously⁸ but eliminating electric quadrupole terms and second order term corrections for nonaxial symmetry ($A_x = A_y = 0.0$ for this case), one finds

$$h\nu = g\beta_0 H + g_0\beta_0 Km_I + g_0\beta_0 m_I^2 F_3^2 / 2H_0, \quad (1)$$

where

$$\begin{aligned} g_1^2 &= g_x^2 \cos^2 \alpha + g_y^2 \sin^2 \alpha, \\ g^2 &= g_1^2 \sin^2 \beta + g_z^2 \cos^2 \beta, \\ g_1^2 A_1^2 &= g_x^2 A_x^2 \cos^2 \alpha + g_y^2 A_y^2 \sin^2 \alpha, \\ g^2 K^2 &= g_z^2 A_z^2 \cos^2 \beta + g_1^2 A_1^2 \sin^2 \beta, \\ F_3^2 &= g_z^2 g_1^2 (A_z^2 - A_1^2)^2 \sin^2 \beta \cos^2 \beta / g^2 K^2, \\ H_0 &= h\nu / g_0 \beta_0, \end{aligned}$$

and β_0 is the Bohr magneton, h is Planck's constant, $g_0 = 2.0023$ is the free electron g factor, and ν is the frequency of the microwave power causing the transitions.

Using this simplified Hamiltonian it was possible to write a program for a TI-58C calculator that varied the parameters until a minimum in the function

$$\sum |H_{\text{exp}} - H_{\text{cal}}| \quad (2)$$

was obtained. The sum is over all experimental points (we used 65), and H_{exp} is the experimentally measured magnetic field position while H_{cal} is that calculated using Eq. (1). The minimum found indicated an average difference between the experimental and calculated values of H to be about 0.75 G. The values of the various parameters obtained in this process are listed in Table I. Figure 2 shows the angular dependence of the spectra for rotations around the three crystalline axes.

TABLE I. Parameters for the NSO_4^{2-} center at RT. Principal directions with respect to the crystalline axes are for two of the four sites. The others are obtained by inversion of the coordinate system.

Tensor	Component		
	<i>x</i>	<i>y</i>	<i>z</i>
<i>g</i>	2.012	2.011	2.007
<i>A</i> (G)	0.0	0.0	25.2

Tensor axis	Crystal axis		
	<i>a</i>	<i>b</i>	<i>c</i>
<i>x</i>	cos 7	± cos 83	0
<i>y</i>	± cos 83	cos 7	0
<i>z</i>	0	0	1

$g_{\text{ave}} = 2.01$
 $A_{\text{iso}} = 8.4 \text{ G}$
 $B_{\parallel} = 16.8 \text{ G}$
 $B_{\perp} = 8.4 \text{ G}$

IV. DISCUSSION

A. Site identification

Because there is an obvious nitrogen hfi splitting one might first think that this center could be localized in a former NH_4^+ ion site. However, as there are two different types of these sites, one would expect the parameters of any center trapped in these two locations to be slightly different. It seems unlikely that any center would be stable in only one of the NH_4^+ sites and not the other. In fact, both NH_3^+ and NH_2^+ were found at both of these sites but with slightly different parameters for each location.^{1,2}

We are thus left with the sulfate ion site or an interstitial site which has the symmetry of the crystal.

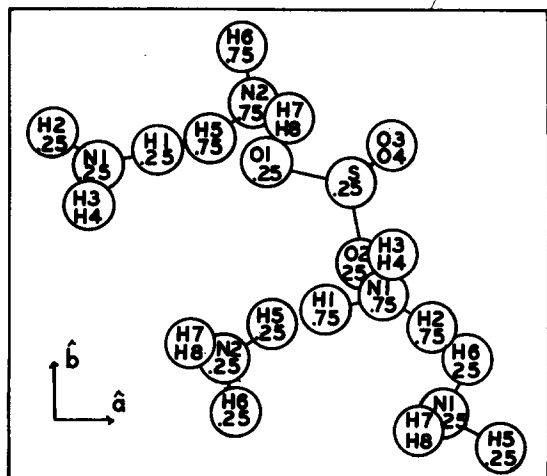


FIG. 1. Illustrative drawing of the $(ij0)$ projection of a typical SO_4^{2-} site in $(\text{NH}_4)_2\text{SO}_4$. The nitrogens are located in two distinct sites; those called type I are labeled N1 and type II are labeled N2. Numerals at atom positions indicate elevation in fractions of the cell edge. H3 and H4 lie ± 0.128 above and below the plane of N1, H1, and H2. H7 and H8 lie ± 0.126 above and below the plane of N2, H5, and H6. O3 and O4 lie at ± 0.2012 above and below the plane of S, O1, and O2. Thus, we have an *ab* mirror plane at 0.25 and 0.75 along the *c* axis.

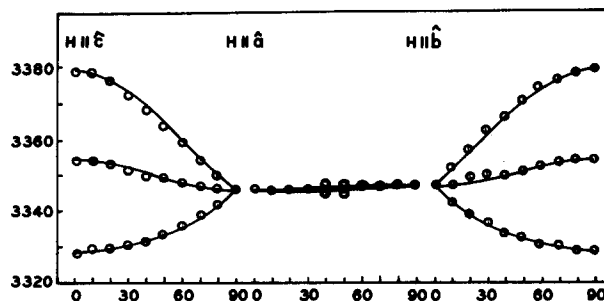


FIG. 2. Angular dependence of the NSO_4^{2-} spectrum as the magnetic field *H* is rotated in planes perpendicular to each of the three crystal axes. Solid curves are those calculated using Eq. (1) and the parameters of Table I, while the circles are the experimentally measured values.

However, because of stability considerations it would seem that the SO_4^{2-} site is the most likely location. In addition, the *x*- and *y*-tensor axis directions have approximately the same directions as the S-O1 atom (about 13° to the *a* axis) and the S-O2 atom (about 8° to the *b* axis) directions, respectively. (See Fig. 1.)

B. Center identification

There is no measurable splitting due to protons so that the nitrogen-hydrogen interaction must be very weak if it exists at all. This immediately eliminates such reported centers as HNSO_3^+ and NH_2SO_3^+ .^{9,10} We are left with a center of the form NSO_n in various states of ionization. $n=3$ must be considered carefully because SO_3^- was produced by *x* irradiation at the same time that NH_3^+ was produced.¹ Many more NH_3^+ centers appeared to be produced (two types of 24 line spectra) than of SO_3^- (a single line spectra of one type). The decay product of these two centers completely eliminates the NH_3^+ center spectra but the SO_3^- is still present but with what appears to be much less intensity. On the other hand, NH_2^+ decays into exactly the same defect center as does NH_3^+ but no SO_3^- was detected at any time during this decay process. Thus, a NSO_3 type defect seems unlikely and a NSO_4 type defect is proposed.

The doubly ionized state of this defect NSO_4^{2-} would explain the great stability of this center (greater than 2 years) as this center would then have an identical charge state to the SO_4^{2-} ion that it replaces and thus might not be very reactive. In addition, the doubly ionized state means that the nitrogen lacks one electron from having full valence orbitals (the sulfur and oxygen are full). This means that the unpaired electron is in a π orbit but acts like a hole center. This explains the positive *g* shift ($g_{\text{ave}} = 2.0099$). In addition, an unsymmetrical local environment lifts the degeneracy of the π_y and π_x orbitals (the *x* direction is along the bond direction) and thus to a first approximation the electron is confined to the π_z orbital (perpendicular to the mirror plane of the crystal). This direction should also have the smallest *g* shift¹¹ as can be seen in Table I.

To a first approximation this center should look much like NO (but with two extra electrons) with the rest of the structure more distant and not affecting the value of the ESR parameters greatly. ClO has the same number of

electrons and thus should show similar characteristics in its ESR parameters. The reported parameters for ClO show that $g_x = g_y = g_z$ and the hfi is zero in the plane perpendicular to the occupied orbital and has a maximum splitting in the direction of this orbital.¹² These characteristics are identical to those reported in Table I for NSO_4^{2-} .

Using the calculated values¹¹ of the isotropic hf coupling (A_{iso}) and the anisotropic coupling (2β) for nitrogen, we can estimate the amount of electron in the s orbital to be $c_s^2 = 0.02$ and that in the p orbital to be $c_p^2 = 0.49$. This indicates that the electron is about 51% on the nitrogen and most of the remaining 49% on the oxygen.

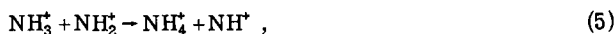
From the accuracy of the data it is impossible to say whether the nitrogen is attached to the O1 oxygen or the O2 oxygen. For the perfect crystal the type II nitrogen and O2 have about the same separation as the type I nitrogen and O1. The remaining type of nitrogen for each case of oxygen is about 6% further from the respective oxygen. Thus, it is entirely possible that we have nitrogens attached at either O1 or O2 and the approximate cylindrical symmetry in the reflection plane masks this information.

C. The radiolysis mechanism

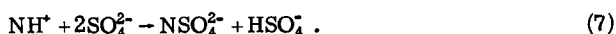
The fact that both NH_3^+ and NH_2^+ decay into the same center indicates that the decay process must involve such things as proton and H-atom transfer before the final state is reached. A study of NH_n^+ ion reactions ($n = 0$ to 4) by Adams, Smith, and Paulson¹³ indicates that there is much bond breaking and bond formation with these ions at thermal energies. In many of the cases the final result is that there is either a proton or H-atom transfer. It thus seems quite reasonable to assume that these NH_n^+ ($n = 1$ to 3) centers can migrate or change form by capturing an H atom from a neighboring NH_n^+ group ($N = 1$ to 4). As each succeeding H atom is less tightly bound to the NH_n^+ group,^{13,14} it is even energetically favorable for the center with fewer protons to give up an H atom to the defect with more protons. The following types of reactions are then suggested to explain the decay of NH_3^+ to NSO_4^{2-} in the x-rayed $(\text{NH}_4)_2\text{SO}_4$ crystal:



This is just the migration of the NH_3^+ defect through the crystal. This probably continues until the NH_3^+ finds another defect and then



Finally,



This last reaction explains the formation of the NSO_4^{2-} defect but also the possible formation of $(\text{NH}_4)\text{HSO}_4$ on a microscopic scale within the bulk $(\text{NH}_4)_2\text{SO}_4$ crystal. This production of $(\text{NH}_4)\text{HSO}_4$ is not unreasonable because $(\text{NH}_4)_2\text{SO}_4$ turns into pure $(\text{NH}_4)\text{HSO}_4$ with the

evolution of NH_3 upon its decomposition at 280°C .¹⁵ These reactions are in agreement with the study of Adams, Smith, and Paulson¹³ which shows that NH_2^+ and NH_3^+ seem to react more readily by H-atom transfer while for NH^+ proton transfer is energetically favorable.

In order to explain the decay of the NH_2^+ center seen on heating the crystal one must assume that the reaction



occurs as it seems very doubtful that NH_2^+ pairs are produced on heating the crystal so that Eq. (6) can be applied immediately. Adams, Smith, and Paulson¹³ have shown that this H-atom transfer from NH_4^+ to a NH_2 group does occur for the case of CH_3NH_2 . Also heating the crystal does not produce enough density of NH_3^+ centers to be detected by ESR so that Eq. (5) can not be used directly to explain the decay. Thus, Eq. (8) is necessary to explain the migration of the NH_2^+ center (or its decay products) so that then the reactions of Eqs. (3)–(7) can become effective in producing NSO_4^{2-} .

D. Low temperature spectra

This NSO_4^{2-} center was also studied at temperatures from RT to temperatures well below the ferroelectric phase transition (this occurs at -50°C). To within the accuracy of our measurements no change in the parameters or symmetry of the NSO_4^{2-} site could be observed. This is not too unexpected because typically hfi are only weakly dependent on the environment and mostly dependent on the type of center itself.¹¹ Also, the small change in the line position with rotation of the crystal would not produce any observable change in the spectra considering the small rotations of the ion groups that apparently occur at the ferroelectric phase transition.^{2,7}

V. CONCLUSIONS

All of the experimental data are in agreement with the identification of this center as NSO_4^{2-} . The decay of both NH_3^+ and NH_2^+ into this same center indicates that the hydrogen bonding in this crystal is very weak and that bond breaking and bond formation takes place quite readily at RT. Because of the insensitivity of this center to its local environment it is impossible to reach any conclusions of what happens at the ferroelectric phase transition from a study of this center.

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