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EPR of the Thermally Produced CrO_4^{3-} in CrO_4^{2-}-Doped $(NH_4)_3H(SeO_4)_2$ Crystals

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Two spin $\frac{1}{2}$ paramagnetic species (species I and species II) are detected by electron paramagnetic resonance (EPR) in CrO_4^{2-}-doped $(NH_4)_3H(SeO_4)_2$ single crystals, after the host crystals had been heated to temperatures well below their decomposition temperature. When heat treated at lower temperatures (≈90°C), only one species (species I) was detected by EPR. The EPR spectrum of this species was identical to that of the CrO_4^{3-} species produced by γ-irradiation of the sample crystals. By comparing the thermal treatment behaviors of the CrO_4^{2-}-doped $Rb_3H(SeO_4)_2$ and $Cs_3H(SeO_4)_2$ crystals, it was established that the electronic defect acquired by the CrO_4^{2-} to form the thermally produced CrO_4^{3-}(I) originates from the NH_4^+ group. It is difficult to determine with certainty from the *g*-values alone the identity of species II. This species could be a CrO_3^- or a Cr^{5+} ion.

Introduction

The electron-excess species of CrO_4^{3-} can be produced in single crystals by several methods: (i) by doping with Cr_2O_3(*1*, *2*) or with CrO_4^{2-} (*3*) during crystal growth from high-temperature solutions; and (ii) by ionizing irradiation of the CrO_4^{2-}-doped crystals (*4*). CrO_4^{3-} has been extensively studied by electron paramagnetic resonance (EPR). The EPR of CrO_4^{3-} in mostly phosphate compounds has been reviewed by Greenblatt (*5*), and in the KH_2PO_4-type ferroelectrics by Dalal (*6*). We report a new method of the production of CrO_4^{3-} in $(NH_4)_3H(SeO_4)_2$ doped with CrO_4^{2-}, by heating the host crystals to temperatures well below their decomposition temperature. Furthermore, by studying the thermal treatment behaviors of the structurally and chemically related $Rb_3H(SeO_4)_2$ and $Cs_3H(SeO_4)_2$ crystals doped with CrO_4^{2-}, the origin of the electronic defect thermally acquired by CrO_4^{2-} in $(NH_4)_3H(SeO_4)_2$ can be ascertained.

$(NH_4)_3H(SeO_4)_2$ is a member of compounds with the general formula $M_3H(XO_4)_2$($M = NH_4^+, K^+, Rb^+$, and Cs^+, and X = S and Se). $(NH_4)_3H(SeO_4)_2$ is known to exhibit a series of successive phase transitions, and among these, the transition at about −92°C is ferroelectric (*7*). The ferroelastic transition at about 29°C has been studied by Kishimoto *et al.* (*8*). Phase transition in $Cs_3H(SeO_4)_2$ has been reported by Komukae *et al.* (*9*). Proton conduction in ammonium compounds and in hydrogen-bonded compounds is a subject of continuing interest. Baranov *et al.* (*10*) have studied the structural phase transitions and

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proton conductivity of $Cs_3H(SeO_4)_2$ and $(NH_4)_3H(SeO_4)_2$ crystals. Wu *et al.* (*11*) have studied by EPR the low-temperature phase transitions and twin-domain structure of $(NH_4)_3H(SeO_4)_2$, by using the doped VO^{2+} and Cu^{2+} ions and the SeO_3^- radical produced by X-irradiation as probes. It is known that in the ammonium containing compounds, the possible charge carriers at high temperatures include an electronic defect, a protonic defect, and migrating cations and anions (*12, 13*). The unpaired electron acquired by CrO_4^{2-} to form the paramagnetic CrO_4^{3-} in $(NH_4)_3H(SeO_4)_2$ is a thermally produced electronic defect, which could contribute to the electrical conductivity of the host crystals at high temperatures. Therefore, by studying the yield of the thermally produced CrO_4^{3-} center, it is possible to gain some knowledge of the temperature dependence of the thermally generated electronic defect in the host crystals.

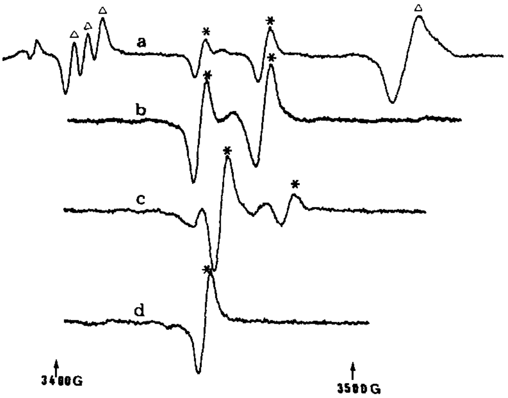

FIG. 1. (a) A typical, room temperature, $H \parallel a$, 9.5-GHz EPR spectrum of thermally produced species I (designated with asterisks) and species II (designated with triangles) in $(NH_4)_3H(SeO_4)_2$ crystals which had been heated at 120°C for 48 hr. (b–d) show the EPR spectrum of the CrO_4^{3-} centers produced by γ-irradiation, for the field parallel to the *a*, *b**, and *c* axes.

Experimental

Single crystals of $M_3H(SeO_4)_2$(M = NH_4^+, Cs^+, and Rb^+) doped with CrO_4^{2-} were grown from aqueous solutions of stoichiometric quantities of M_2SeO_4 and H_2SeO_4 at 20°C. $(NH_4)_3H(SeO_4)_2$ doped with CrO_4^{2-} crystallizes in the form of thin hexagonal plates. When viewed in polarized light, a conoscopic image characteristic of uniaxial crystals can be observed. The sample crystals were of a single domain. Chemical analysis of the nitrogen content was consistent with the samples being $(NH_4)_3H(SeO_4)_2$. By contrast, $(NH_4)_3H(SeO_4)_2$ crystals, doped with Cu^{2+} and grown at 40°C, show an uniaxial interference figure at first, which, after some time at room temperature, develops mosaic domain patterns consisting of a large number of small domains. $(NH_4)_3H(SeO_4)_2$ undergoes a ferroelastic transition at about 29°C (*8*), with the simultaneous appearance of twin domains. Above this transition, the crystal structure is trigonal with the *R*3*m* space group, while below this transition it is monoclinic with the *A*2/*a* space group (*8*). The twin domain structure in the monoclinic *A*2/*a* phase has been studied by Kishimoto *et al.* (*8*) and by Wu *et al.* (*11*).

The heating of the sample crystals was carried out inside a programmable furnace, at temperatures between 90–230°C. The EPR spectrometer used is an ER 200 D Bruker spectrometer, operating at about 9.5 GHz. The spectrometer is equipped with a single-axis goniometer, a Bruker liquid nitrogen, continuous-flow cryostat and temperature controller and a Hewlett–Packard 5343A microwave frequency counter.

Results and Discussion

Figure 1a shows an EPR spectrum observed at room temperature, from an $(NH_4)_3H(SeO_4)_2:CrO_4^{2-}$ crystal heated at 120°C for 48 hr, for the magnetic field parallel to the *a* axis of the hexagonal lattice. Crystals so heated did not show any visible sign of thermal decomposition. Two chemically inequivalent $S = \frac{1}{2}$ paramagnetic species were thermally produced; one of these is designated as species I (indicated by asterisks in Fig. 1a) and the other as species II (indicated by triangles in Fig. 1a). When heated at 90°C for 94 hr, a weak EPR spectrum of species I can be detected, but the species II spectrum is absent. When heated at 120°C or at higher temperatures, both species can be simultaneously detected. Furthermore, the yield of species II relative to that of species I increases with the thermal treatment temperature, and this indicates that species I is the precursor of species II. Both species can be detected by EPR in sample crystals heated at 215°C for 2 hr (sample crystals so heated did not show any visible damage). When heated at 230°C for 2 hr, the sample crystals became a polycrystalline mass glued to the ceramic container. In other words, these two thermally produced $S = \frac{1}{2}$ species remain chemically stable, even when the host crystals are heated to the highest permissible temperature.

To evaluate the spin Hamiltonian parameters, sample crystals were aligned in the microwave cavity such that they could be rotated about the *a*, *b**, and *c* axes. The *a* and the *c* axes refer to the crystal axes of the hexagonal lattice for the trigonal $R\bar{3}m$ phase, and the *b** axis is mutually perpendicular to both the *a* and *c* axes. The observed rotation patterns (taken at every 5°) for rotations about the three axes are shown in Figs. 2 and 3.

The rotation patterns shown in Figs. 2 and 3 can be analyzed by assuming that the paramagnetic species is of spin $\frac{1}{2}$. For an $S = \frac{1}{2}$ paramagnet, the rotation patterns can be analyzed by the effective *g*-factor of the form (*14*)

$$g_{\text{eff}} = (l^2T_{xx} + m^2T_{yy} + n^2T_{zz} + 2lmT_{xy} + 2mnT_{yz} + 2nlT_{zx})^{1/2}, \quad (1)$$

where T_{ij} is the square of the *g*-matrix which is assumed to be symmetric, and *l, m, n* are the directional cosines of the field with respect to the reference axes of *a*, *b**, and *c*. The number of possible magnetically inequivalent sites asociated with each paramagnetic species is determined by the Laue symmetry of the host lattice (*15, 16*). The maximum number of magnetically inequivalent sites is six for the trigonal $R\bar{3}m$ phase. But since the *a* axis is observed as a principal axis for the *g*-tensor, magnetic degeneracy results, with the consequence that the six sites become pairwise degenerate. The patterns shown in Figs. 2–3 can be so analyzed, and the evaluated principal *g*-values and the directional cosines of the principal axes are listed in Table I. The *g*-values of both of the thermally produced $S = \frac{1}{2}$ species related to Cr(V) indicate that its orbital ground state is composed mainly of the $3d_{x^2-y^2}$ orbital.

These two thermally produced $S = \frac{1}{2}$ species could be the tetrahedral CrO_4^{3-} complex ion, or the CrO_3^- ion, or the Cr^{5+} ion. If the species are of the CrO_3^- or the Cr^{5+} variety, then it would imply a molecular dissociation of the doped CrO_4^{2-} ion. To distinguish between these, we have investigated the paramagnetic species produced by γ-irradiation. Figures 1b–1d show the EPR spectrum detected at room temperature in a crystal irradiated with a total dosage of ca 5 Mrad. The *ab**, *b***c*, and *ca* patterns for this γ-ray-produced, $S = \frac{1}{2}$ species are identical with those shown by the thermally produced species I. It is known that the Cr(V) oxyanions of CrO_4^{3-} and CrO_3^- can be produced by X-ray or γ-ray irradiation. Therefore, the thermally produced species I can be identified as either one of these two species. It has been pointed out by Dalal and Maple (*17*) that it is difficult to distinguish between these two Cr(V) oxyanions simply from the evaluated *g*- and hyperfine tensors alone. They have proposed that by measuring the temperature dependence of the EPR linewidth, a distinction between these two may be made. We have measured the temperature dependence (300–100 K) of the peak-

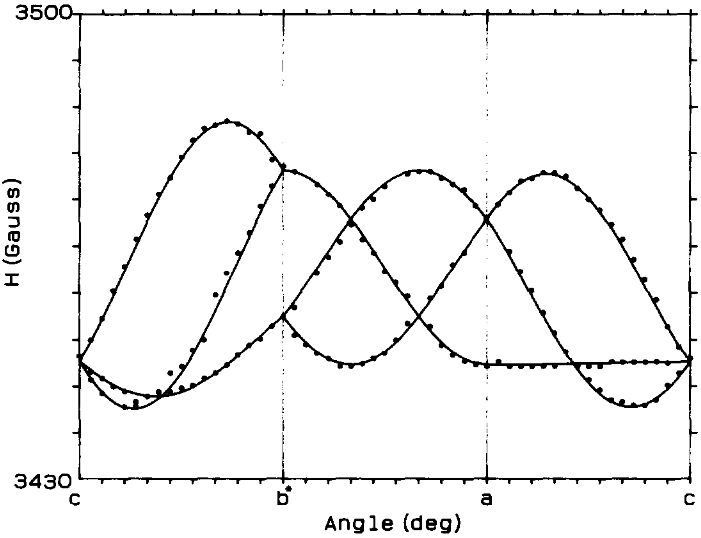

FIG. 2. Observed and fitted b^*c, ab^*, and ca rotation patterns for the thermally produced CrO$_4^{3-}$(I) center. The CrO$_4^{3-}$ center produced by γ-irradiation showed identical patterns.

to-peak linewidth (ΔH) of the two thermally produced species. Species I showed a monotonic increase in ΔH with the decrease in temperature; $\Delta H = 3.2$ G at 295 K and 5.2 G at 111 K. Species II showed a slightly monotonic increase inΔH with the decrease in temperature; $\Delta H = 4.0$ G at 295 K and 4.4 G at 111 K. Therefore, species I is more sensitive to temperature. However, the temperature dependence behavior of the ΔH of

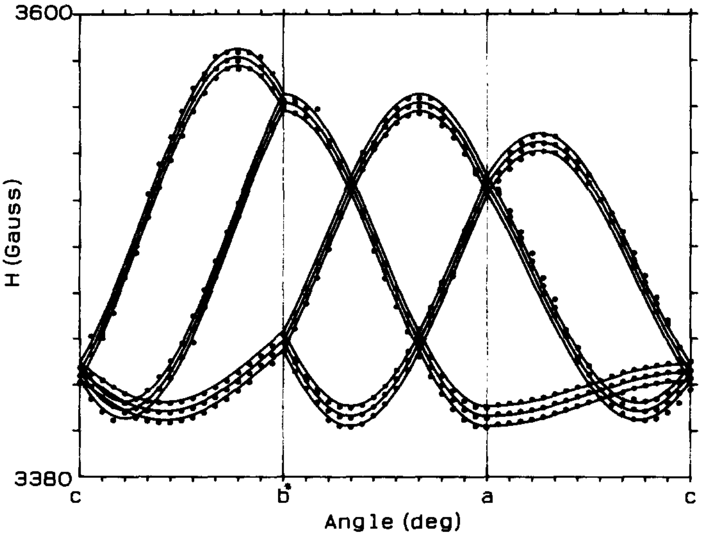

FIG. 3. Observed and fitted b^*c, ab^*, and ca rotation patterns for the thermally produced species II.

TABLE I

THE EVALUATED PRINCIPAL *g*-VALUES AND THE DIRECTIONAL COSINES OF THE PRINCIPAL AXES FOR THE TWO THERMALLY PRODUCED Cr(V) SPECIES

Species	Principal *g*-values and their direction cosines	Principal nitrogen hyperfine constants (G)
I	1.977 : [1,0,0]	
	1.947 : [0,0.913,0.408]	
	1.971 : [0,0.408, −0.913]	
II	1.990 : [1,0,0]	
	1.895 : [0,0.939,0.344]	4.7, 4.0, 4.5
	1.989 : [0,0.344, −0.939]	

species I indicates that spin-lattice relaxation is not the primary source of its ΔH. Thus, the relaxation method (*17*) may not be applicable in this experiment.

For the following reasons, we believe that the thermally produced species I is a CrO_4^{3-} species rather than a CrO_3^- species. First, species I is the initial or primary thermally produced $S = \frac{1}{2}$ species. We have found that, when heated at 200°C for 2 hr, $Cs_3H(SeO_4)_2$ and $Rb_3H(SeO_4)_2$ crystals doped with CrO_4^{2-} did not show any thermally produced, $S = \frac{1}{2}$ species related to the Cr(V) oxyanions or Cr(III) species (the same is true for thermal treatments at lower temperatures). This eliminates the acid hydrogen as the reducing agent for the conversion of Cr(VI) to Cr(V) for species I, and points to the ammonium group as the responsible reducing agent. Thus, if species I is a CrO_3^- species, then it would imply a partial molecular dissociation of the doped CrO_4^{2-}. Such a reaction can be regarded as an ammonium-hydrogen-assisted reaction of the type

$$CrO_4^{2-} + 2H^+ + e^- \rightarrow CrO_3^- + H_2O. \quad (2)$$

The reaction product could also be an OH^- radical instead of H_2O, and in which event only one proton is needed in the chemical reaction. The proton, H^+, and the electron, e^-, in Eq. (2) could belong to a local NH_4^+ group or a protonic defect and an electronic defect released by an NH_4^+ group,

$$NH_4^+ \rightarrow NH_3^+ + H^+ + e^-. \quad (3)$$

Such an NH_4^+ group could be either local or nonlocal to the chromate ion. If the proton and the electron participating in the reaction are thermally generated point defects, then it can be assumed that by thermal treatments at lower temperatures (such as 90°C), CrO_4^{3-} can be produced (CrO_4^{2-} has exibited a strong affinity to electron), which should be the initial thermally produced Cr(V) oxyanion: it can be assumed that when thermally treated at lower temperatures, the chromate oxygens are insufficiently thermally excited to chemically react (according to Eq. (2)) with their local NH_4^+ groups. Then, as the temperature of heat treatment is raised, one might expect fo find progressively the CrO_3^-, the Cr^{5+}, and eventually the Cr^{3+} species. Based on such considerations, we identify species I as a CrO_4^{3-} species.

After the completion of this work, we have recently experimentally observed the processes just described in M_2SnCl_6(M = NH_4^+ and K^+) crystals doped with CrO_4^{2-} (the details will be published separately). We have found that when heat-treated at lower temperatures (less than about 150°C), the initial thermally produced paramagnetic species is an $S = \frac{1}{2}$ species. The principal *g*-values of this species are 1.996, 1.969, and 1.910, which are comparable to those of species II in $(NH_4)_3H(SeO_4)_2$ (see Table I). However, such crystals when subsequently heated to temperatures close to their decomposition temperature exhibited two chemically inequivalent Cr(III) EPR spectra, and the EPR spectrum of the initially produced $S = \frac{1}{2}$, Cr(V) species can no longer be detected. When a K_2SnCl_6 crystal (which is isomorphous with $(NH_4)_2SnCl_6$) doped with CrO_4^{2-} was heated to temperatures as high as 400°C, neither the Cr(III) species nor the Cr(V) oxyanion species can be detected by EPR. However, when the $K_2SnCl_6 : CrO_4^{2-}$ crystals were codoped with a nominal 2 mole% of $(NH_4)_2SnCl_6$, they did show an

EPR spectrum of a thermally produced $S = \frac{1}{2}$ species identical to that in $(NH_4)_2SnCl_6:CrO_4^{2-}$ crystals. The K_2SnCl_6 result is significant, for it shows that the electronic defect thermally acquired by the CrO_4^{2-} originates from a nonlocal NH_4^+ group via a mechanism represented by Eq. (3). These results also support our conclusion that species I in $(NH_4)_3H(SeO_4)_2$ is a CrO_4^{3-} rather than a CrO_3^- species.

We next discuss the site symmetry of the γ-ray-produced or the thermally produced CrO_4^{3-}(I) species. A detailed crystal structure of $(NH_4)_3H(SeO_4)_2$ is at present unknown. However, its sulfate analog, $(NH_4)_3H(SO_4)_2$, has exhibited a sequence of successive phase transitions (*18, 19*) similar to that of $(NH_4)_3H(SeO_4)_2$. Among these, $(NH_4)_3H(SO_4)_2$ undergoes a transition from a trigonal $R\bar{3}m$ phase to a monoclinic *A2/a* phase at about 140°C. The crystal structure of the monoclinic *A2/a* phase has been analyzed by Suzuki and Makita (*20*). In this structure, the sulfate tetrahedra are all chemically equivalent, and the sulfate oxygens are hydrogen-bonded to the acid proton and the ammonium protons. The recent work of Wu *et al.* (*11*) contributes to a further understanding of the crystal structures of the trigonal and the low-temperature monoclinic phases of $(NH_4)_3H(SeO_4)_2$. They have detected by EPR only one chemically inequivalent SeO_3^- radical in X-irradiated $(NH_4)_3H(SeO_4)_2$ crystals in the trigonal and the monoclinic phases, which suggests that the selenate tetrahedra are all chemically equivalent in the known phases of this compound. Furthermore, in the trigonal $R\bar{3}m$ phase, the SeO_3^- radical exhibits axial symmetry with the symmetry axis pointing parallel to the trigonal axis of the host crystal, which suggests that the selenate tetrahedron possesses trigonal symmetry and that Se occupies a lattice site of $3m$ point symmetry similar to those of the sulfate tetrahedron in the trigonal phase of $(NH_4)_3H(SO_4)_2$. That only one chemically inequivalent CrO_4^{3-} species was thermally produced (CrO_4^{3-}(I)) or γ-ray produced is consistent with the selenate tetrahedra as being all chemically equivalent in $(NH_4)_3H(SeO_4)_2$ (*11*). It is reasonable to assume that the doped CrO_4^{2-} ion substitutes for SeO_4^{2-}. The point symmetry at the Cr(VI) site would then be $3m$. The CrO_4^{3-} species produced either by γ-ray irradiation or by thermal treatment has displayed nearly axial symmetry, but the symmetry axis is not aligned parallel to the trigonal axis of the host lattice. However, the *a* axis of the hexagonal lattice is observed as a principal axis of the *g*-tensor for species I and II. Assuming that this magnetic symmetry has its origin in crystal point symmetry, then it suggests that this CrO_4^{3-}(I) species is associated with a local vacancy (most probably an acid-proton vacancy) located on one of the three vertical mirror planes passing through the Cr site.

Species II in $(NH_4)_3H(SeO_4)_2$ shows a 1 : 1 : 1, three-line hyperfine pattern (see Fig. 1a), which can be construed as due to a hyperfine coupling of the unpaired electron to a single nitrogen nucleus. Considering the circumstances under which this species is thermally produced, we suggest that this nitrogen nucleus is located at a partially dissociated or completely dissociated NH_4^+ group, but we have been unable to establish a more concise model. Based on *g*-values alone, this Cr(V) species could be one of the following three $S = \frac{1}{2}$ species: a CrO_4^{3-}, a CrO_3^-, or a Cr^{5+} species. The fact that this species is not produced by γ-ray irradiation (note that the selenate tetrahedra, and by inference the chromate tetrahedra, are all chemically equivalent in the host lattice) and that it has the CrO_4^{3-}(I) as precursor suggests that it is either a CrO_3^- or a Cr^{5+} ion. Chou and Yu (*21*) have recently investigated by EPR the reduction by thermal heating of the γ-ray-produced Cr(V) oxyanions into Cr(III) species in single crystals of $LiCsSO_4$ (codoped with NH_4^+), $LiNH_4SO_4$, and $(NH_4)_4SO_4$. They have found that after heat treatment at about 80°C, the Cr(V) → Cr(III) reduction can be detected by EPR, and that after heat treatment at about 200°C, this reduction is complete. In light of these, the stability exhibited by the thermally produced CrO_4^{3-} (I) and species II in $(NH_4)_3H(SeO_4)_2$ is unusual. (For this reason, we hesitate to definitely identify species II as either the CrO_3^- or the Cr^{5+} species.) We feel that this difference in the stability of the Cr(V) oxyanions in $(NH_4)_3H(SeO_4)_2$ and in the sulfate compounds (*21*) may be related to the differences in proton affinity among SeO_4^{2-}, SO_4^{2-}, CrO_4^{2-}, CrO_4^{3-}, and CrO_3^-.

Conclusions

Two chemically stable spin $\frac{1}{2}$ species are detected by EPR in CrO_4^{2-}-doped $(NH_4)_3H(SeO_4)_2$ crystals heated to temperatures well below the decomposition temperature of the host compound. Species I, which alone is thermally produced via heat treatment at lower temperatures and which has displayed an EPR spectrum identical to the $S = \frac{1}{2}$ species produced by γ-ray irradiation, can be identified as a CrO_4^{3-} species. By contrast, no thermally produced $S = \frac{1}{2}$ or $S = \frac{3}{2}$ species can be detected by EPR in the chemically and structurally related compounds of $Cs_3H(SeO_4)_2$ and $Rb_3H(SeO_4)_2$ doped with CrO_4^{2-}. This suggests that the unpaired electron thermally acquired by the doped CrO_4^{2-} in $(NH_4)_3H(SeO_4)_2$ originates from the NH_4^+ group. The second thermally produced, $S = \frac{1}{2}$, Cr(V) species, which could be either a CrO_3^- or a Cr^{5+}, is more difficult to identify with certainty.

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