

Local Structure and Tunneling Kinetics of Ammonium Aluminum Alum by Infrared Hole-Burning

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The title compound, crystallized with a few percent of deuterium, contains some NH_3D^+ and HOD. At low temperatures, five N–D stretch bands are observed. These belong to two ammonium sites with apparent C_s symmetry in the low-temperature phase. The N–D bands can be hole-burned with an infrared laser. Burning bands belonging to the A-sites transforms some of them to the higher-energy B-sites. The A- and B-sites probably differ from each other by the arrangement of water and sulfate about the ammonium.

I. Introduction

The alums form a large family of double salts having the general formula $\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$. M^{I} is a monovalent ion, M^{III} is a trivalent ion, and X is either S or Se.¹ Six of the water molecules are octahedrally coordinated to the trivalent ion. The other six water molecules are loosely coordinated about the monovalent ion. The water molecules and the sulfate ions form a complicated hydrogen-bonded network. All the alums crystallize in the cubic space group $P\bar{a}3$ (No. 205) (T_h)⁶ but are of at least three types (α , β , and γ) characterized by subtly different arrangements of the water molecules around the monovalent ion and different positions for the sulfate ions. Although diffraction studies of the alums have been done since 1934,² the details of the structure remain a topic of current study.³ Two problems make the structure of the alums a particular challenge: (1) the high-temperature phases show disorder;³ (2) there often are low-temperature phases. These are of lower symmetry and may well be disordered as well. At any rate, the structures of most of the low-temperature phases are unknown.

The ammonium alums are of particular interest. The ammonium ion contributes new degrees of freedom—the orientation of the ion—to the already complex alum structure. Many of these low-temperature phases are ferroelectric.⁴ The diffraction methods and electrical measurements determine overall symmetry as well as other global properties. In addition, many of the alums have been studied by techniques that determine the properties of a given ion and its immediate surroundings. These include electron paramagnetic resonance of some of the metal ions such as chromium,⁵ nuclear magnetic resonance of the hydrogen-containing species such as ammonium,⁶ and nuclear-quadrupole resonance of the quadrupolar nuclei such as the deuterium in D_2O .⁷

We apply a new technique to this problem. We have found that ammonium compounds doped with a small amount of

deuterium to form some NH_3D^+ ions can be “hole-burned” in the infrared.⁸ In this process, the sample, which is held at a low temperature, is irradiated by an infrared source at the position of an N–D stretching band. The radiation causes the ammonium ion to rotate and results in a spectral hole at the position of the irradiated N–D stretch. Antiholes are formed at the position of the other possible N–D stretch bands. Usually, the ammonium ions tunnel back to their original orientational distribution on annealing in the dark, and the spectrum reverts to its original appearance. The hole-burning technique provides an assignment of the N–D stretches and information on the strength of the associated hydrogen bonds and of the barriers between the various ammonium ion orientations.

In this paper, we consider mainly the ammonium aluminum alum (AmAl), $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Crystals of the ammonium alums are closely related to the ammonium Tutton salts, $(\text{NH}_4)_2\text{M}^{\text{II}}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, which hole-burn easily and which we have studied extensively. In contrast to the Tutton salts, the alums show phase transitions, disorder, and, for the low-temperature phases, unknown crystal structures that make our results more difficult to interpret. We examine the spectra of the related alums, AmCr and RbAl, to aid in our assignments.

The AmAl crystallizes as an α -type alum at room temperature (RT). The sulfate ions are disordered with the two possible orientations related by inversion,⁹ as is also the case with many other alums.³ The ammonium ions are also disordered in two possible orientations.^{10,11} Correlation between the sulfate and the ammonium orientations has not been directly determined nor do the water molecules appear to be disordered.¹⁰ A phase transition occurs in the AmAl from a paraelectric to a ferroelectric phase with a transition temperature, T_c , variously estimated to be in the range 60–80 K.^{4,5,12,13} The crystal structure in the ferroelectric phase is unknown.

II. Experiment

The three alums, AmAl, AmCr, and RbAl, were each prepared by dissolving equimolar amounts of the appropriate sulfates in hot water

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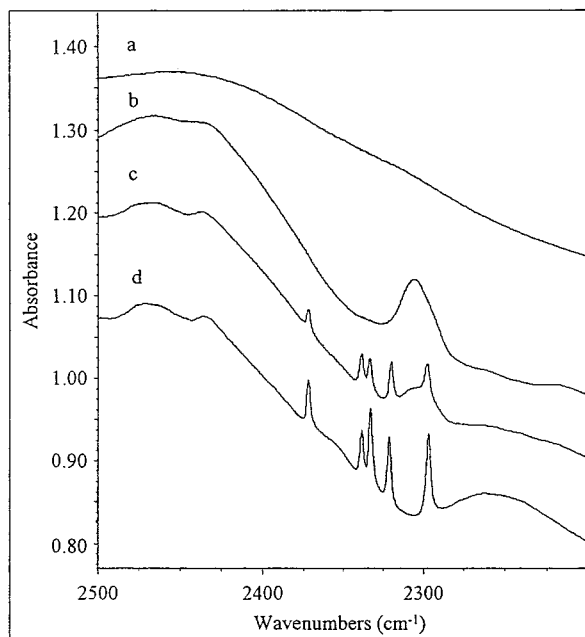


Figure 1. Infrared absorption spectra of ammonium aluminum alum containing a few percent of deuterium: (a) RT; (b) 85 K; (c) 80 K; (d) 10 K.

containing a small amount of D₂O. The alums crystallized out as the solutions cooled. The crystals were washed with ethanol and dried, milled with mineral oil, and then spread between two salt plates.

Infrared spectra of the sample were obtained in the 2200–2500 cm⁻¹ region using a Nicolet 850 Fourier transform infrared spectrophotometer with an InSb detector. The CaF₂ plate sandwich containing the sample was put into a closed-cycle helium cryostat (CTI-Cryogenics SC 21). A Si diode thermometer was mounted in an OFHC Cu holder close to the sample plates. The temperature was regulated to ±0.5 K at low temperature and to ±5 K at high temperature using a temperature controller (Lakeshore Cryotronics DTC 500-SP).

The difference-frequency laser system is described in our previous experiments.¹⁴ A mask with a 1.5 mm hole was placed over the sample so that the infrared beam from the difference-frequency laser system passed through the sample coaxial with the broadband infrared beam from the FT-IR spectrometer.

Infrared spectra of the NH₃D⁺Al-alum between two KBr plates were observed in the 1500–600 cm⁻¹ region with the same spectrophotometer using an MCT detector and no mask.

III. Results

A. Spectra. When deuterium is introduced into the crystal, some of the deuterium goes into the ammonium ion to produce NH₃D⁺ ions while some goes into the water to produce HDO. In Figure 1, only one broad band is observed in the 2200–2500 cm⁻¹ region at RT. When the temperature is lowered, three bands are observed at 2307, 2441, and 2464 cm⁻¹. The lowest frequency peak is attributed to N–D, while the two higher frequency ones are attributed to O–D. A weak shoulder on the lower-frequency side of a broad band is discernible at RT and becomes evident on cooling. Below 80 K, five new bands appear in the infrared absorption spectra at 2297, 2321, 2333, 2339, and 2372 cm⁻¹.

Since there is no assignment reported in the literature for the infrared spectra of AmAl below *T_c*, we use the deuterium-doped AmCr and RbAl to compare with the NH₃D⁺Al-alum. AmCr has a structure very similar to that of AmAl.¹⁰ The radii of the NH₄⁺ and Rb⁺ ions are almost the same, and the structure of

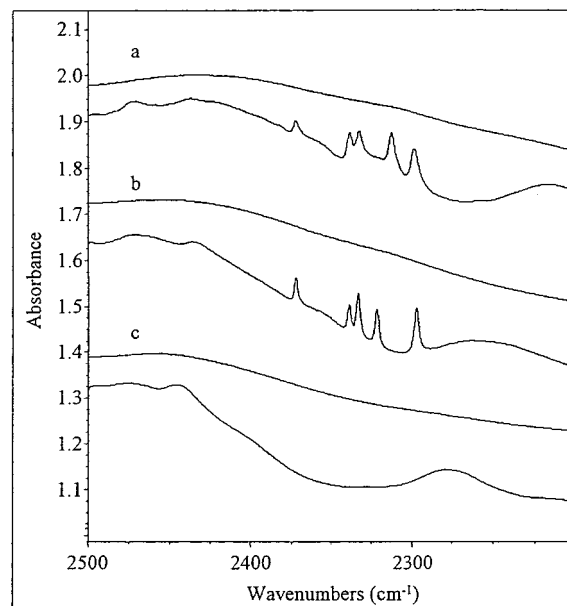


Figure 2. Comparison among the spectra of deuterium-doped (a) ammonium chromium alum, (b) ammonium aluminum alum, and (c) rubidium aluminum alum. The upper spectrum of each set is measured at RT, and the lower spectrum is measured at 10 K.

RbAl is also very similar to that of AmAl.⁹ The doped RbAl-alum has only O–D bands, while the NH₃D⁺Al-alum has both N–D and O–D bands. In Figure 2, we show the infrared spectra of the AmCr-alum and the RbAl-alum and compare them to the spectra of the AmAl-alum at both high and low temperatures. Parts a, b, and c of Figure 2 present the spectra of the doped AmCr, AmAl, and RbAl, respectively. The upper spectrum of each set is measured at RT, and the lower spectrum is measured at 10 K. The RT spectra of the three different samples are almost the same. However, the lower temperature spectra are different, as expected. The AmCr and AmAl spectra (parts a and b of Figure 2) show five bands in the 2250–2400 cm⁻¹ region, while the RbAl spectrum in Figure 2c does not show any narrow bands. We conclude that all five bands in the 2250–2400 cm⁻¹ region are N–D bands.

B. Temperature Dependence. The bands that appear in the spectrum as the temperature is lowered through *T_c* persist but change with temperature. Figure 3 shows spectra taken at different temperatures, and Figure 4 plots the peak heights at these temperatures. Once the temperature has been lowered to 10 K, the spectrum takes considerable time to come to equilibrium. Figure 5 shows two 10 K spectra, one taken immediately on reaching 10 K and one taken about 14 h later. The figure also shows the difference between these two spectra. The peak heights are plotted as a function of time in Figure 6 (note that the *x*-axis (time) is reversed to compare with that in Figure 4). The spectra at 10 K take about 2 days to reach equilibrium. The sample is cooled from high temperature to 10 K with the intensities plotted in Figure 4. At 10 K, the spectrum is taken after 1 day, and it is from this spectrum that the values in Figure 4 are taken. If the sample is left at 10 K, it continues to decay, and this is plotted in Figure 6. The left-hand side of Figure 4 and the right-hand side of Figure 6 are identical. Note that with both temperature and time, bands II and IV change together as do bands III and V. This is in accord with our assignment (see below) that bands II and IV belong to site B and bands III and V to site A. Band I, which changes the least, has two components, one belonging to site A and one to site B.

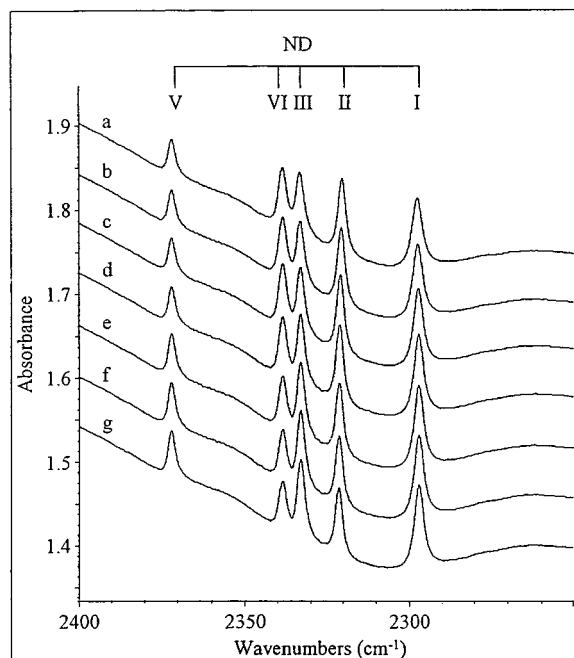


Figure 3. Infrared absorption spectra of deuterium-doped ammonium aluminum alum as a function of temperature at (a) 70, (b) 60, (c) 50, (d) 40, (e) 30, (f) 20, and (g) 10 K.

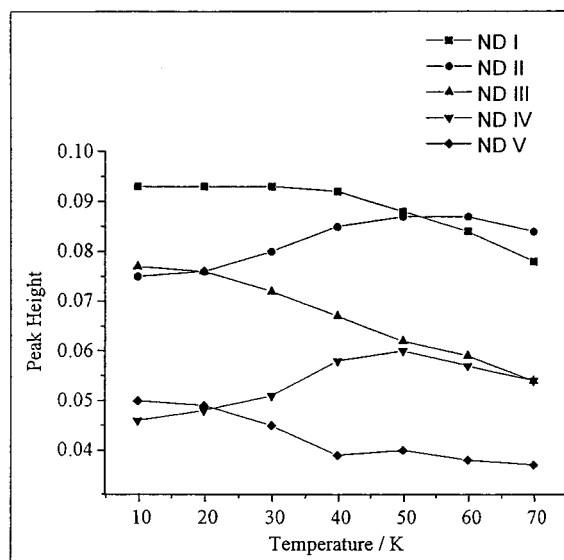


Figure 4. Change of the peak heights of each band in the infrared spectrum with temperature.

C. Hole-Burning. We systematically burned each of the N–D bands and show the infrared difference spectra of the $\text{NH}_3\text{D}^+\text{Al}$ -alum at 10 K in Figure 7. Infrared irradiation at the position of N–D band I (2297 cm^{-1}) causes a decrease in the intensity of N–D band I, forming a “hole”, and increases in the other bands forming “antiholes” (Figure 7a). Irradiating each of the bands in turn gives different patterns of holes and antiholes. Note that burning N–D band V causes a hole at both N–D bands I and V, and this is due to complex relaxation paths among molecules with their N–D bonds in different orientations. Some properties of the bands and holes are listed in Table 1. The hole width (full width at half-height, fwhh) of each hole is about the same as the fwhh of the corresponding absorption band. The decays of the holes and antiholes formed on irradiating each N–D band are shown in Figure 8. In Figure 8, the bands at 2328 and 2348 cm^{-1} are uncompensated absorption

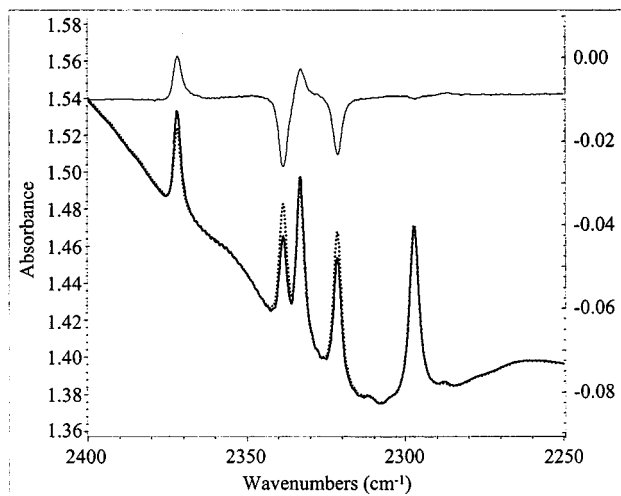


Figure 5. Difference spectra of ammonium aluminum alum at 10 K. The upper spectrum is the difference between a spectrum taken at 14 h (continuous line) and that taken just after the temperature is lowered (dotted line). The difference spectrum is referenced to the right-hand scale, and the original spectra are referenced to the left-hand absorption scale.

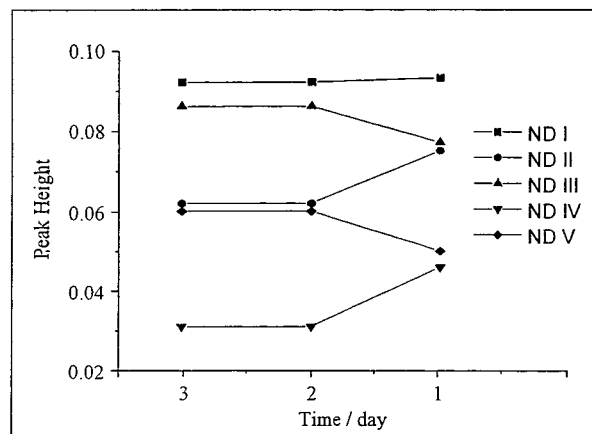


Figure 6. Change of the peak heights of each band in the infrared spectra at 10 K with time. Note that the x -axis scale is reversed for comparison with Figure 4.

by condensed N_2 and CO_2 , respectively, in the optical path. The behavior of the holes and antiholes formed in N–D band I is different from the behavior of those in the other bands. All of the holes and antiholes decay monotonically except for those of N–D band I, which show more complicated behavior (Figures 8 and 9). Figure 8 shows that the initial hole in band I changes to an antihole (which must then decay eventually). Figure 9 shows the N–D band I antihole on an expanded scale from the irradiation of N–D band IV. The antihole changes position with time, blue-shifting by about 2 cm^{-1} .

Figure 10 shows the decay of the holes and antiholes for bands II–V. The decays are divided into two sets with bands III and V decaying with a time constant of about 11 h, whereas bands II and IV decay in about 40 h.

D. Assignment. Both the temperature-dependent and time-dependent spectra suggest that there are two NH_3D^+ sites in the low-temperature phase of AmAl-alum. Irradiating N–D band I (Figure 7a) gives one hole (hole I) and two antiholes (holes III and V) that produce further holes in bands II and IV before decaying, hole I turning into an antihole in the process. We postulate two ammonium sites, one which we call site A giving rise to bands I, III, and V, and the other which we call

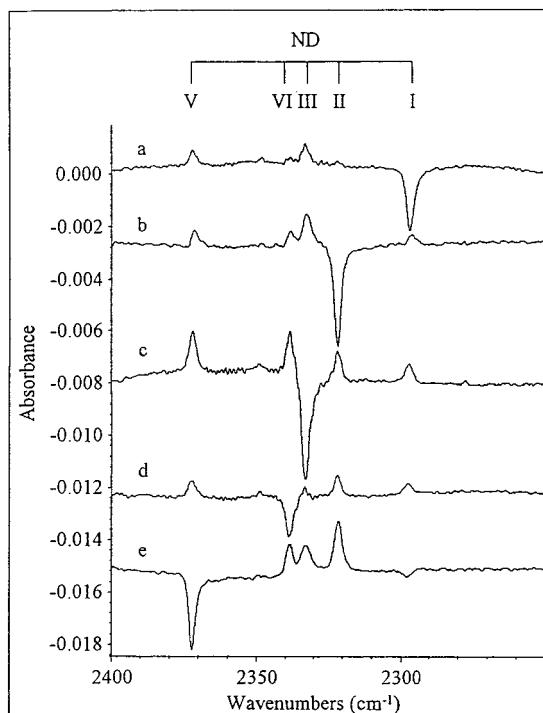


Figure 7. Infrared hole-burning difference spectra of ammonium aluminum alum before and after 30 min irradiation at 10 K with the infrared laser frequency at (a) 2297, (b) 2321, (c) 2333, (d) 2339, and (e) 2372 cm^{-1} .

Table 1. Properties of the Bands and Holes in Deuterium-Doped Ammonium Aluminum Alum at 10 K

band no.	band		hole		
	width ^a (cm^{-1})	area ^b	width ^a (cm^{-1})	area ^c (%)	slope (10^{-4} min^{-1})
I	6	0.234	6	4.08	
II	5	0.128	5	9.86	-1.85 ± 0.80
III	6	0.141	6	9.00	-7.95 ± 0.61
IV	3	0.064	4	6.24	-1.84 ± 0.83
V	4	0.104	5	8.18	-5.66 ± 0.53

^a fwhh. ^b Arbitrary units. ^c As a percentage of the original band area.

site B giving rise to bands I, II, and IV as listed in Table 2. Site B is the higher-energy site with more intensity at high temperature and the one preferentially depleted on infrared irradiation. The rotations in the dark of the NH_3D^+ ions and their transfer from site A to site B are complicated multistep processes involving tunneling and take various periods of time. The time constant for the decay of the holes is about 11 h for the A-sites and about 40 h for the B-sites (Table 1).

Mid-infrared spectra of the hydrogen and deuterium-doped AmAl-alum are shown in Figure 11. Some years ago, the spectra of the high-temperature phase were studied at RT and at 100 K and assigned.¹⁵ As with the spectra in Figure 11, the various bands sharpened as the temperature was lowered and there is either considerable hysteresis or no abrupt change at T_c . The bands at about 1100 cm^{-1} are the asymmetric stretch (ν_3) of the sulfate ion. Some of the bands of the NH_3D^+ can be identified from our assignments of ammonium stearate containing NH_3D^+ .¹⁶ Thus, the bands at about 1300 cm^{-1} are the symmetric deformation (ν_4). We have found HND deformations of the related moiety NH_2D^+ in glycine hydrochloride in the

region from 970 to 1100 cm^{-1} and from 790 to 830 cm^{-1} , and this suggests that the bands we see at about 1000 cm^{-1} and at about 800 cm^{-1} are also NH_3D^+ deformations.¹⁷

IV. Discussion

At room temperature, the ammonium aluminum alum is disordered as already mentioned. It has been argued that the disorder is due to large-amplitude motion rather than static disorder.¹⁸ Whatever the case, it is not surprising that the N–D and O–D bands show only broad, poorly defined absorptions. As the temperature is lowered, there is an abrupt change in the spectra at about 80 K. We did not try to define the transition temperature with precision because the transition has been observed to have considerable hysteresis and to vary with the substitution of deuterium for hydrogen. NMR and dielectric studies suggest that the water motion slows with temperature with an activation energy of 29 kJ/mol in both the high-temperature and low-temperature phases, whereas the ammonium motion is believed to freeze out at the transition temperature.¹⁹ Our spectra (Figure 2) agree with this general picture with the appearance of broad O–D and sharp N–D bands at low temperature.

Although many of the alums become ferroelectric at low temperature, the small polarization of the AmAl has left its ferroelectricity questionable.⁴ However, recent experiments show ferroelectricity unambiguously.¹² Electron paramagnetic resonance studies of Cr^{3+} -doped AmAl show orthorhombic symmetry. This observation, together with the existence of ferroelectricity, severely restricts the possible symmetry of the low-temperature phase. The $m\bar{3}$ (D_{3d}) point group of the $Pa\bar{3}$ high-temperature phase must transform to the lower symmetry, $mm2$ (C_{2v}), in the lower-temperature phase.

This still leaves a number of different space groups as possibilities. However, the crystal structure of one alum, methylammonium aluminum alum (MeAmAl) has been determined.²⁰ This has a RT symmetry of $Pa\bar{3}$ and a low-temperature symmetry of $Pca2_1$ (No. 29); the latter belongs to $mm2$ as required. Although the MeAmAl must differ from the AmAl in some respects, we will use it as a model. The orthorhombic low-temperature MeAmAl crystal forms from the RT crystal without breaking, and this suggests that the atoms do not move far in the process. The unit cell parameters are $a = 12.57 \text{ \AA}$, $b = 12.33 \text{ \AA}$, $c = 12.38 \text{ \AA}$ for the orthorhombic phase and 12.50 \AA for the cubic phase, each containing four formula units.

A comparison of the crystal sites in the cubic and orthorhombic structures requires a displacement of the coordinates to match the conventional origin used for two space groups.²⁰ Note that the high-temperature $Pa\bar{3}$ symmetry is obtained by considering the methylammonium as a point molecule, which, of course, implies disorder.²¹ The sites in the high-temperature phase are 4 Al atoms in site a (S_6), 4 CH_3NH_3 ions in site b (S_6), 8 SO_4 ions in site c (C_3), and 48 water molecules in sites of C_1 symmetry. In the low-temperature structure in $Pca2_1$, all the sites are in general positions and have C_1 symmetry, so the sulfate sites must split into 2 inequivalent sites and the water molecules into 12.

In our experiments, we see NH_3D^+ in two inequivalent sites, each with three N–D stretch bands. This implies sites of C_3 symmetry (or near symmetry) in which two of the N–D

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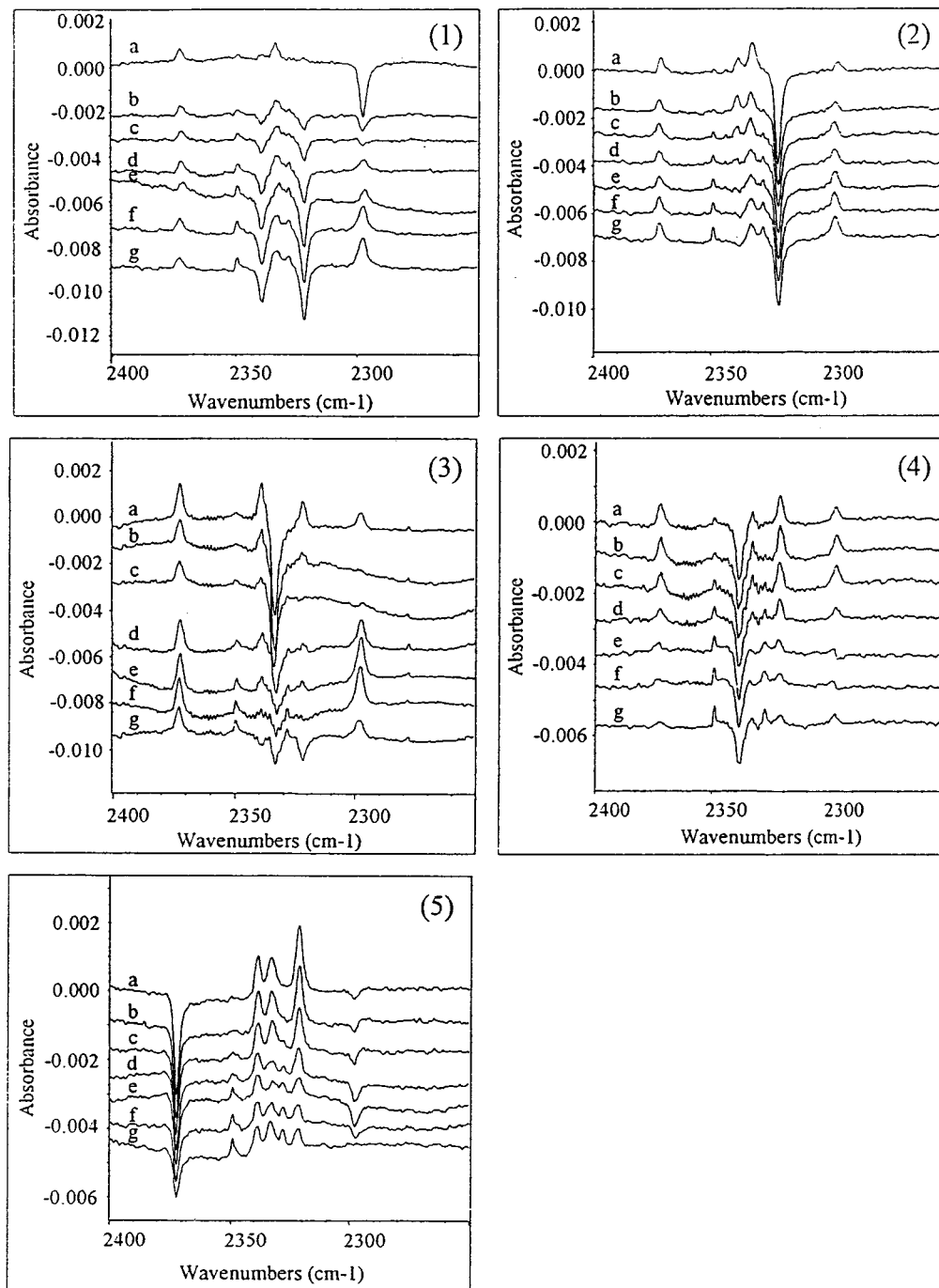


Figure 8. Decay of the infrared difference spectra at 10 K following irradiation (1) at N–D band I, (2) at N–D band II, (3) at N–D band III, (4) at N–D band IV, and (5) at N–D band V: (a) 0 min; (b) 90 min; (c) 180 min; (d) 270 min; (e) 360 min; (f) 450 min; (g) 540 min.

positions are equivalent (Table 2). There are two sites with different energies and different spectral positions; these can change into each other on irradiation. At this point, we note that the sulfate ions are disordered in the RT phase. The sulfate and ammonium ions probably remain hydrogen-bonded, and a change in position of the one is accompanied by a change of position in the other. In the low-temperature phase, the two distinct ammonium sites will be distinguished by different orientations of the sulfate surroundings. Excitation of an N–D stretch rotates the NH_3D^+ ion, and the propagating strain in the crystal then moves the sulfates. This latter process changes the site from an A-site to a B-site.

We have seen this type of change in one other crystal—the low-temperature phase of ammonium trifluoromethanesulfonate

(ammonium triflate).²² In ammonium triflate, there is a high-temperature phase of relatively high symmetry obtained by disordering the various moieties among different positions. A low-temperature phase forms, but its crystal structure has not been determined. We see two NH_3D^+ sites, which transform into each other on hole-burning. Like the alum, hole-burning the A-sites eventually produces holes in the higher-energy B-sites. For the triflate, the ammonium sites can differ by the position of the neighboring trifluoromethyl or sulfonate groups.

We have further information on the alum because the relaxation times of a number of its electrical and magnetic properties have been measured. However, the positions and

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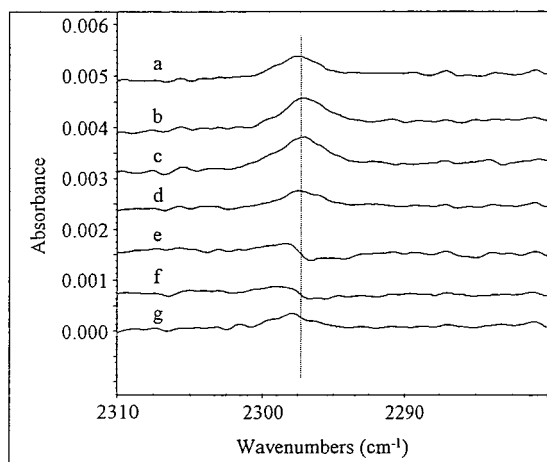


Figure 9. N–D band I part of the spectra in part 4 of Figure 8 on an expanded wavenumber scale. In this figure, it is clear that the position of the maximum peak changes with decay time. The dotted line shows the original position of N–D band I.

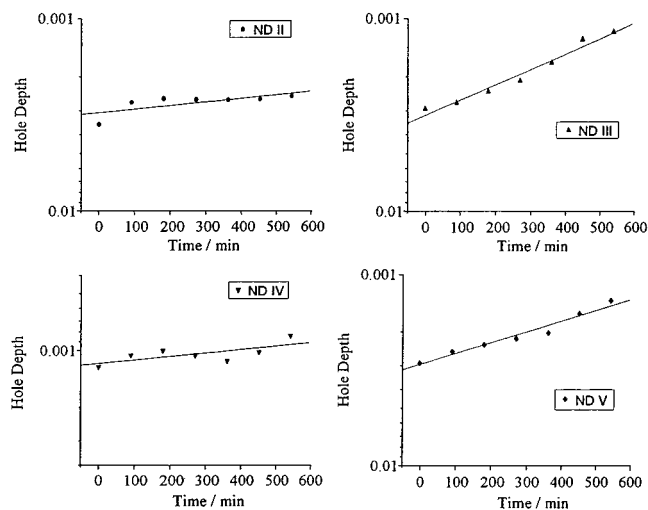


Figure 10. Recovery of the holes on a log scale as a function of time at 10 K. Note that the decay of the bands III and V is faster than the decay of bands II and IV with time constants of 11 and 40 h, respectively (Table 1).

Table 2. Assignment of N–D Vibrational Stretching Bands in Deuterium-Doped Ammonium Aluminum Alum

band no.	wavenumber/cm ⁻¹	identification
I	2297	A ₁ A ₂ B ₁ B ₂
II	2321	B ₃
III	2333	A ₃
IV	2339	B ₄
V	2372	A ₄

orientations of the water and sulfate ions of the low-temperature phase of the AmAl are unknown as is the orientation of the ammonium ion. Each of these can relax, and each contributes differently to a given measurement such as the dielectric constant or NMR line width. We briefly summarize some of the previous measurements to get a complete picture of the infrared hole-burning and filling process.

The dielectric relaxation time in the high-temperature phase varies over a 10⁹ range of times as $\ln \tau = \ln \tau_0 - E_a/(RT)$ with an E_a of about 12 kJ/mol.⁵ Over this range of times, the widths and shapes of the electron paramagnetic resonance spectra of Cr-doped AmAl change, making comparison difficult. In the lower-temperature phase, the Cr ions exist in a number of sites

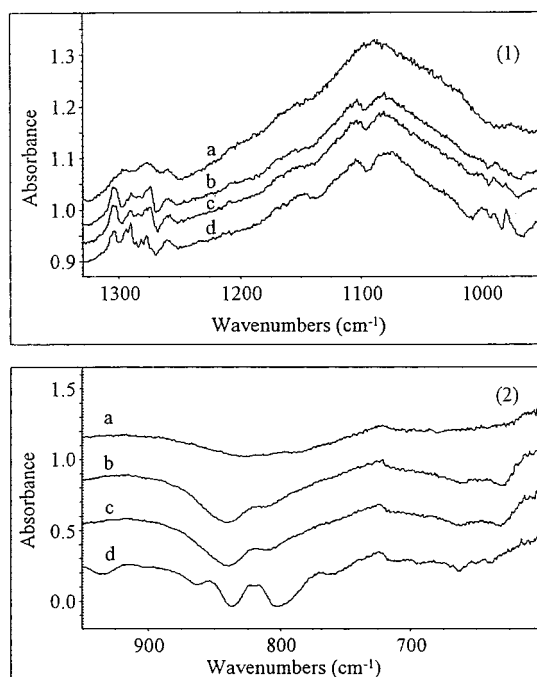


Figure 11. Infrared absorption spectra of deuterium-doped ammonium aluminum alum (a) in the 1330–950 cm⁻¹ region and (2) in the 950–600 cm⁻¹ region: (a) RT; (b) 85 K; (c) 80 K; (d) 10 K.

whose relative population varies with the rate of cooling of the crystal, an observation that implies frozen-in disorder.

NMR measurements of the NH₄⁺ protons yield 10.7 kJ/mol as the activation energy for the ammonium reorientation.⁶ Other dielectric measurements show an activation energy of 9.0 kJ/mol¹² and an 18 K temperature range for the hysteresis loop. Recent EPR measurements give activation energies of 13 kJ/mol above 210 K and 4.6 kJ/mol from 210 K to about 125 K.²³ The difference in energy between sulfate orientations has been determined for KAl to be about 2 kJ/mol.²⁴

The overall picture shows a number of ions reorienting in the AmAl-alum and similar crystals with activation energies of about 10 kJ/mol and energy differences between conformations of a fraction of that. As already mentioned, the actual motion probably involves rearrangement of a number of ions at a time. Most of the dynamic data are for the high-temperature phase, and we can expect higher barriers and slower motion in the low-temperature phase. The time constants we observe for the hole-filling of 11 and 40 h are consistent with barriers in this range.²⁵ We cannot make a more accurate comparison without an estimate of the reduced mass for the motion.

V. Conclusion

The detailed structure of ammonium aluminum alum remains only partially determined. The high-temperature phase is disordered. The low-temperature phase is a distorted lower-symmetry version of the higher-temperature structure, but the positions and orientations of the ammonium, sulfate, and water may still be disordered. We can burn holes in the N–D stretch bands, showing that the ammonium ions are held with barriers to reorientation of about 10 kJ/mol. The hole burning identifies the N–D bands as belonging to two separate N–D sites A and B. Each site has 2-fold symmetry, and each shows three stretch

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bands. Hole-burning of NH_3D^+ ions makes the three bands of a given site change relative intensity, as expected. However, site A can change into site B. This must occur by a change in position or orientation of the neighboring water or sulfates and is similar to a process we have observed in other crystals. At 10 K the decay of the holes occurs by tunneling and the decay of 10s of hours is consistent with barriers of about 10 kJ/mol.

Experiments covering a wider time range and experiments that establish correlation such as 2-D NMR may uncover more

of the nature of the low-temperature phase. However, diffraction experiments may be particularly difficult because the low-temperature phase may have frozen-in disorder as do the high-temperature phases of many of the alums.³

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