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Effects of Pressure on the Chemical Properties of Solid Surfaces. V. The Surface Acidity of the Compressed Aluminum Sulfate

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In order to clarify the mechanism of the acidity change due to compression, aluminum sulfate was compressed under various pressures ranging from 0 to 4200 kg/cm^2 and at a temperature of 20, 65, or 80°C, and the surface acidity and the structure of these samples were measured. It was found that the acidity change due to compression was proportionate to the protonic acid. Lewis acid was made to appear only by heating the sample at temperatures higher than 90°C. Further, for the purpose of increasing the surface acidity, the compression of the sample at lower temperatures was found to be more effective than the compression at higher temperatures. In addition to the spectroscopic data, the results of DTA and TGA experiments supported the idea that the observed acidity change resulted from the distortion of the structural unit of aluminum sulfate.

In the previous works[1-3] which treated the effects of pressure on the chemical properties of solid surfaces, the present authors have found that the surface acidities of various metal sulfates vary on compression. In these works the acidity change was discussed in terms of the change in the crystal structure as well as in terms of the change in the water content in the sample. However, the discussion was only qualitative, and the details of the mechanism of the acidity change due to compression could not be clarified. Therfore, the present authors have undertaken a new series of experimental works designed to clarify the mechanism of the acidity change.

In the present work, aluminum sulfate octadecahydrate was used as a sample. The surface acidity was measured by a conventinal titration method. The structural changes due to compression were investigated by means of infrared spectroscopy, far-infrared spectroscopy, Raman spectroscopy, differential thermal analysis, and so on. In this paper, the details of the experimental results will be presented and the relation between the acidity change and the structural change will be discussed.

Experimental

Material. Commercial aluminum sulfate octadecahydrate was used as the raw material of sample.

Preparation of the Sample. The raw sulfate was compressed by the procedures described in the previous papers.[1-3] The compression was carried out under various pressures, ranging from 0 to 4200 kg/cm^2, and at a desired temperature of either 20, 65, 80°C. In every case, pressure was applied over a 10-min period. The resulting cyclindrical pellet, 6 mm in diameter and 2 mm in height, was pulverized in a mortar. The pulverized material was subjected to drying in vacuum for 45 min at a temperature of 18°C. The resulting dry material served as a sample for the desired measurements. In order to minimize the effects from the change in ambient conditions, compressions, pulverizings, dryings and weighings were carried out in an air-conditioned room.

For the sake of convenience, the samples which were subjected to the compression at 20, 65, and 80°C were defined as P_{20}, P_{65}, and P_{80} respectively. Then, for instance, $P_{65,4200}$ means the sample which was compressed under a pressure of 4200 kg/cm^2 and at a temperature of 65°C.

Surface Acidity. The surface acidity was determined by Benesi's method[4] with the following four indicators: dicinnamalacetone ($pK_a = -3.0$), benzeneazodiphenylamine ($pK_a = 1.5$), *p*-diphenylaminoazobenzene ($pK_a = 3.3$), and phenylazonaphthylamine ($pK_a = 4.0$). The acidity measurements were also carried out in the air-conditioned room.

Qualitative Tests for Lewis Acid. In order to identify Lewis acid on the sample powder, the color of the sample surface was observed by adding phenolphthalein or trithylchloride as an indicator. That is, a given amount of the sample powder was transferred to a 50-m*l* conical flask containing 10 m*l* of purified benzene. Then, several drops of a 0.1 % benzene solution of an indicator were added and color of the sample surface was observed.

Surface Areas. The specific surface area of the sample was evaluated by applying the BET theory to the adsorption data of nitrogen at −195°C.

Water Content. The content of aluminum in a given amount of the sample powder was determined by a conventional gravimetric analysis, and on the basis of these results the water content in the sample was calculated.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). DTA and TGA runs were carried out on a Rigaku Denki Thermoflex R-8000 unit. The DTA curves and the TGA curves were obtained at a temperature programming rate of 5°C/min.

X-Ray Diffraction. Powder X-ray diffraction patterns of the sample were obtained with a Shimadzu GX-1 X-ray Diffractometer. The Cu$K\alpha$ radiation (Ni filter) at 30 kV and 15 mA was used. The sample powder was coated with a collodion film to prevent interference from air moisture.

Infrared and Far-infrared Spectroscopy. The infrared spectra for the 400—4000-cm^{-1} wave number range were obtained with Perkin-Elmer Model 125 and Perkin-Elmer Model 337 Infrared Spectrophotometers. A Hitachi FIS-3 Infrared Spectrophotometer was used to obtain spectra for the 30—400-cm^{-1} wave number range.

A nujol technique was employed in every case except when the spectra for the O–H stretching vibration was obtained. In the latter case, a chlorobutadiene technique was employed.

Raman Spectroscopy. The Raman spectra of the sample powder were obtained with a Ūkigōsei RL-II Spectroscope.

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[1] Y. Ogino, and T. Kawakami, This Bulletin, **38**, 972 (1965).

[2] Y. Ogino, T. Kawakami, and K. Tsurumi, *ibid.*, **39**, 639 (1966).

[3] Y. Ogino, T. Kawakami, and T. Matsuoka, *ibid.*, **39**, 859 (1966).

[4] H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

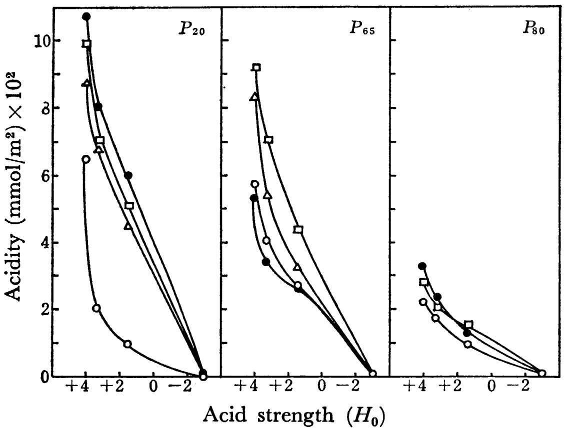

Fig. 1. Acid strength distribution curves for aluminum sulfate samples compressed under various conditions.
(○) $P_{T,0}$; (□) $P_{T,1400}$; (△) $P_{T,2800}$; (●) $P_{T,4200}$

Results

Surface Acidity. Acid-strength distribution curves for aluminum sulfate samples compressed under various conditions are given in Fig. 1, where the acidity values per unit of surface area are indicated as a function of the H_0 value. As can be seen in this figure, the surface acidity for every sample of P_{20}, P_{65}, and P_{80} increased on compression. Further, it can be said that a lower compacting temperature is preferable in order to increase the acidity value within the range of $H_0 = -3.0$—$+1.5$.

Identification of Lewis Acid. As can be seen in Table 1, none of the samples compressed at temperatures lower than 80°C showed any sign positive to the existence of Lewis Acid. Therefore, it might be concluded that only protonic acid appeared on compression. On the other hand, the color test (Table 1) against the samples which had been dehydrated at 89—104°C showed that Lewis acid appeared on the surface of the sample.[5]

Water Content. The water contents in the samples treated under various conditions are given in Fig. 2.

Table 1. IDENTIFICATIONS FOR LEWIS ACID

Compacting condition	Indicator	
	Phenolphthalein	Trithylchloride
$P_{20,0-4200}$	No color	No color
$P_{65,0-4200}$	No color	No color
$P_{80,0-4200}$	No color	No color
$T=80$	No color	
$T=90$	Pink (faint)	
$T=108$	Pink	
$T=128$	Pink (deep)	
$T=155$	Pink (deep)	

☐ : Samples heated at various temperatures without compression. For example, $T=80$ means the sample heated at 80°C and at zero compacting pressure.

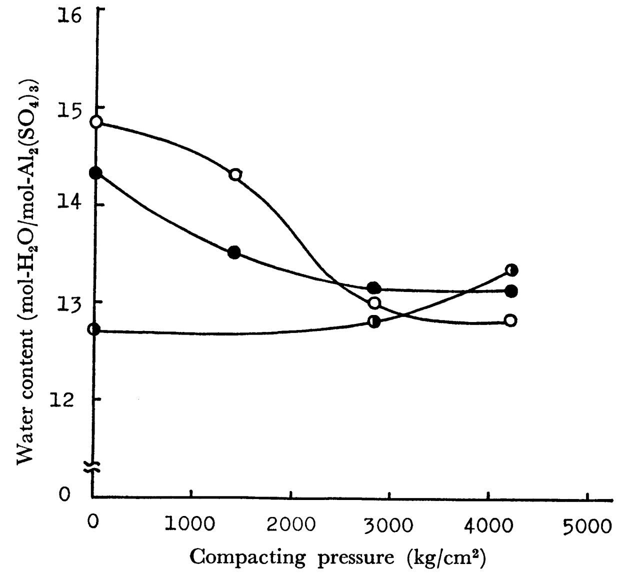

Fig. 2. Relations between the compacting pressure and the water contents in the samples compressed at various temperatures: (○), P_{20}; (●), P_{65}; (◑), P_{80}

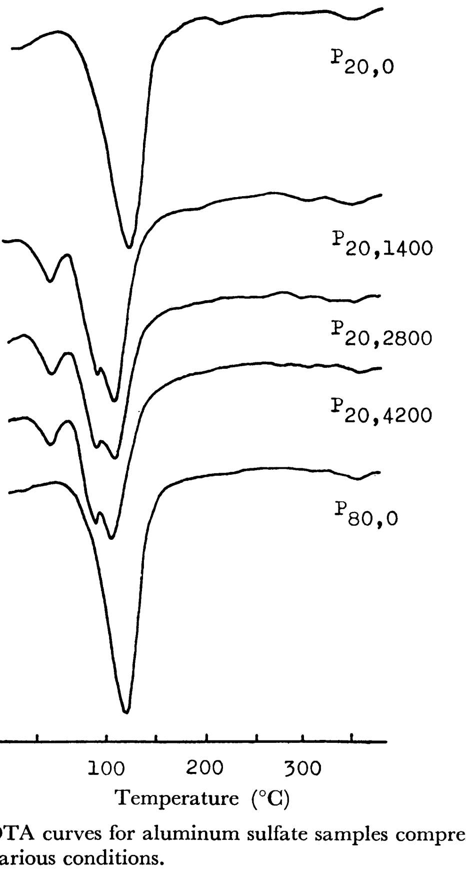

Fig. 3. DTA curves for aluminum sulfate samples compressed under various conditions.

DTA and TGA. DTA curves for several samples are given in Fig. 3. On the basis of a comparison of this figure with the results of the chemical analysis of water and the TGA data, the DTA endothermic peaks were attributed to the dehydration processes from the sample. For example, an endothermic peak appearing at 59°C for the $P_{20,0}$ sample was attributed to the desorption of the physically-adsorbed water.

Further, from the results of TGA it was found that

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[5] H. P. Leftin and W. K. Hall, "Actes Congr. Intern. Catalyse, 2^e", Paris, 1960, p. 1352 (1961); G. Kortum, J. Vogel, and W. Braun, *Angew. Chem.*, **70**, 561 (1958).

the amount of dehydratin at 89—104°C from each sample was as follows:

$P_{20,0}$	12.3 mol-H_2O/mol-$Al_2(SO_4)_3$
$P_{20,1400}$	12.3 mol-H_2O/mol-$Al_2(SO_4)_3$
$P_{20,2800}$	12.3 mol-H_2O/mol-$Al_2(SO_4)_3$
$P_{20,4200}$	12.3 mol-H_2O/mol-$Al_2(SO_4)_3$

It must be noted that these values were approximately equal to 12.

In addition to the above-mentioned fact, the DTA data revealed another interesting fact. A marked difference between the DTA curve for the uncompressed sample and that for the compressed sample was observed. That is, an original endothermic peak which had appeared at 89—104°C in the uncompressed sample split into two endothermic peaks in the compressed sample.

X-Ray Diffractions. The Powder X-ray diffraction patterns for the various samples are given in Fig. 4. These patterns prove that the aluminum sulfate used in this study consisted of crystals of octadecahydrate, hexadecahydrate, and tetradecahydrate. From the low intensity of the diffraction peaks for the tetrahydrate, the content of this hydrate in the sample seemed to be small.

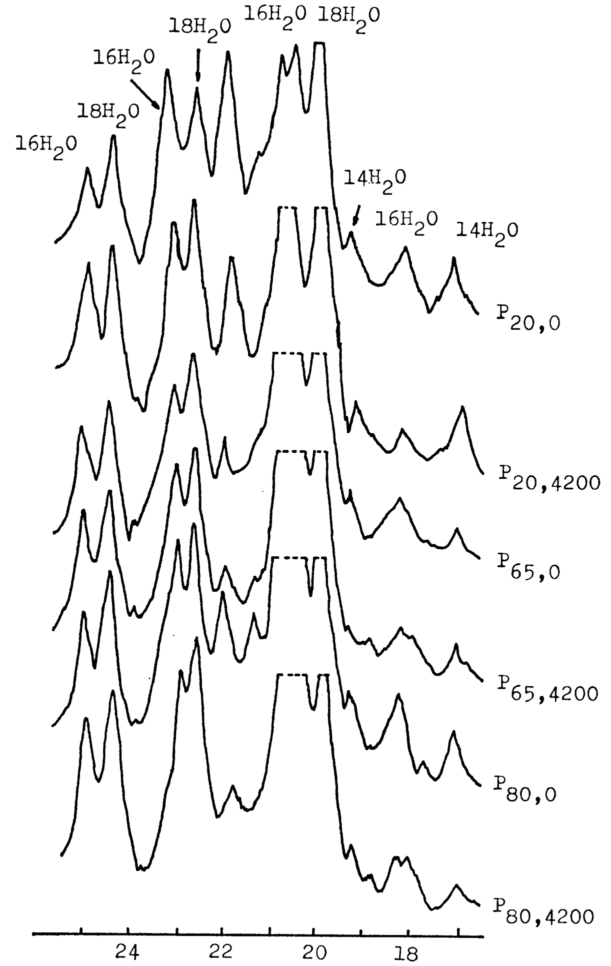

Fig. 4. X-Ray diffraction patterns for aluminum sulfate samples compressed under various conditions.

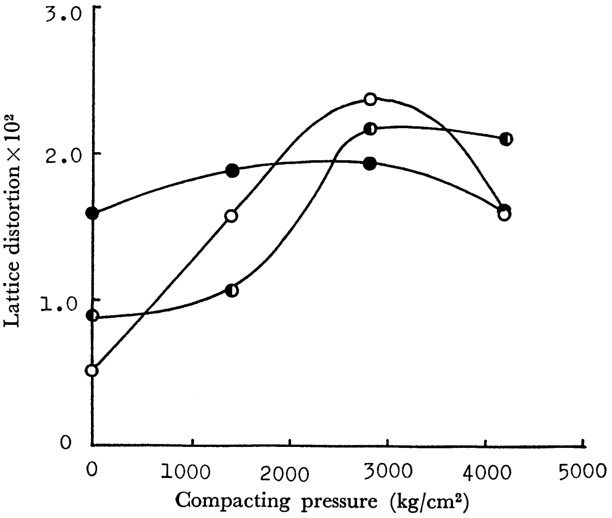

Fig. 5. Relations between the lattice distortion and the compacting pressure: (○) P_{20}; (◐) P_{65}; (●) P_{80}

The degree of lattice distortion calculated by applying Hall's method[6] to the X-ray diffraction data is given in Fig. 5. As can be seen in this figure, the degree of lattice distortion for octadecahydrate was proved to increase with the increase in the compacting pressure, except for the P_{80} sample.

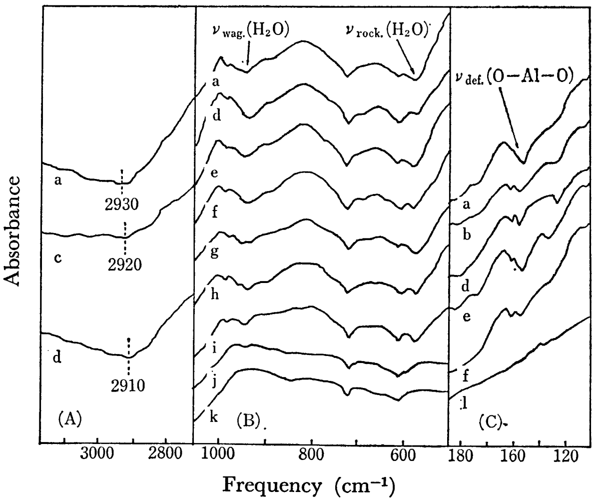

Fig. 6. Infrared and far infrared spectra for alumimun sulfate samples compressed under various conditions: ((a) $P_{20,0}$; (b) $P_{20,1400}$ (c); $P_{20,2800}$; (d) $P_{20,4200}$; (e) $P_{65,0}$; (f) $P_{65,4200}$; (g) $P_{80,0}$; (h) $P_{80,4200}$) and for the samples heated at various temperatures without compression: ((i) 90°C; (j) 130°C; (k) 155°C; (l) 105°C)

Infrared Spectra and Far-infrared Spectra. The infrared spectra of samples prepared under various conditions are given in Fig. 6. Among the absorption bands in this figure, the bands assigned to both ν_{OH} and ν_{O-Al-O} were found to vary on compression. The details of the change in the absorption spectra are given below.

i) On the compression of the sample, the peak position of a broad band ranging from 2500 cm^{-1} to 3500

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[6] W. H. Hall, *Proc. Phys. Soc.*, **A62**, 741 (1949).

cm^{-1}, which was assigned to the OH stretching vibration[7], shifted to lower frequencies—*i.e.* $P_{20,0}$: 2930 cm^{-1}, $P_{20,2800}$: 2920 cm^{-1}, $P_{20,4200}$: 2910 cm^{-1}.

ii) The band appearing at 155 cm^{-1} for the uncompressed sample was assigned to the O–Al–O deformation.[8] When the sample was compressed, the original 155 cm^{-1} band split into two peaks (Fig. 6); this splitting was more marked in the $P_{20,4200}$ sample than in the $P_{65,4200}$ sample.

iii) As can be seen in the Fig. 6 (i), the heating of the uncompressed sample at 90°C resulted in a decrease in the intensities of the absorption for both $\nu(H_2O)_{rock.}$ and $\nu(H_2O)_{wag.}$.
A further increase in the heating temperature resulted in the almost complete disappearance of these absorption bands (Fig. 6, j,k).

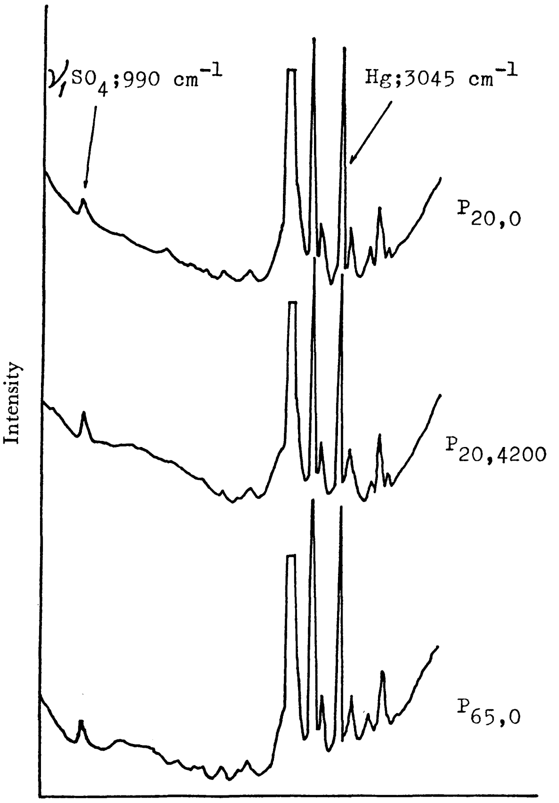

Fig. 7. Raman spectra for aluminum sulfate samples compressed under various conditions.

Raman Spectra. The Raman spectra for several samples are given in Fig. 7. The line which appeared at 990 cm^{-1} was assigned to the ν_1 vibration of sulfate ions in the sample. The relative intensity of this line against the intensity of the line for mercury (3045 cm^{-1}) is given in Table 2.

TABLE 2. RELATIVE INTENSITY OF THE RAMAN ν_1 LINE FOR SO_4^{-2}

Compacting condition	Relative intensity
$P_{20,0}$	7.0×10^{-2}
$P_{20,4200}$	12.8×10^{-2}
$P_{65,0}$	9.3×10^{-2}
$P_{65,4200}$	9.3×10^{-2}

Discussion

Acidity Change on Compression. Similar to a previous work,[1] the present reseach revealed that the surface acidity of aluminum sulfate hydrate varies on the compression of the sample. Furthermore, in the present study it was found that the degree of the acidity change due to compression was a function of the compacting temperature. This fact suggests that the surface acidity might be controlled by changing the compacting temperature as well as the compacting pressure. With respect to this point, it seems to be important that the degree of the acidity change was larger when a lower compacting temperature was employed.

The acidity which appeared on the compressed sample could not be referred to Lewis acid of a high strength, the acidity was referred to protonic acids with a strength of $H_0 \geq -3.0$. The experimental results shown in Table 1 indicate that Lewis acid was made to appear only by heating the sample to a temperature higher than 90°C. Since the compression was carried out below 80°C, it is natural to consider that the observed acidity on the compressed sample surface would have a protonic character.

Surface Areas, Water Contents, and Acidity Changes. The acidity change observed in the present study must be related to the change in the structure of the aluminum sulfate sample. However, the acidity change could not be explained by a simple structural change. For instance, the surface area of the sample varied also on compression, but this change was not proportional to the observed acidity change. That is, the surface acidity per unit of surface area varied also on compression. Moreover, the observed acidity change due to compression was not proportional to the degree of dehydration from the sample.

Crystal Structure and Acidity Changes. On the basis of the experimental results on the X-ray diffraction as well as on the water content of the sample, it was thought that the hydrates in the sample have nonstoichiometric compositions with respect to water. That is, the results of the X-ray diffraction study showed that the sample contains aluminum sulfate octadecahydrate, aluminum sulfate hexadecahydrate, and a small amount of aluminum sulfate tetradecahydrate. Therefore, the water content in the sample should be larger than 14 mol-$H_2O/Al_2(SO_4)_3$. However, as was shown in the previous section, the results of the chemical analysis showed that the water content in the sample was less than 14 mol-$H_2O/Al_2(SO_4)_3$. This discrepancy seems to show that the water content in each of the observed hydrates has a smaller value than the corresponding formular value.

The nonstoichiometric water content may produce distortions of the crystal structure of the aluminum sulfate hydrate. Indeed, the distortion of the crystal lattice of the sample was found to be considerable, as is shown in Fig. 5. Thus, the lattice distortion was suspected of causing the acidity change.

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[7] I. Gamo, This Bulletin, **35**, 1055 (1962).

[8] H. J. Prask and H. Boutin, *J. Chem. Phy.*, **45**, 3289 (1966).

Unfortunately however, examinations based on this suspicion showed that the correlation between the observed acidity change and the degree of lattice distortion was incomplete. That is, the acidity change was found to be proportional to the degree of lattice distortion only for a series of samples made at a given compacting temperature; a change in the compacting temperature resulted in a change in the proportionality constant. Thus, the correlation was incomplete. Therefore, the observed lattice distortion can not be considered as the primary factor which determines the surface acidity.

Structural Unit for Aluminum Sulfate Hydrate. Considering the observed nonstoichiometric water content as well as the works of Gamo,7) Prask,8) and Taylor,9) the model given in Fig. 8 (A) was adopted as a structural unit of aluminum sulfate hydrate. According to this model, there are 12 mol of coordinated-water (I) per unit of $Al_2(SO_4)_3$. In the present study, it was assumed that the water (I) could not be removed by compression, though the anion-water (II) could be removed by compression. Therefore, the number of moles of the anion-water (II) was thought to be variable and capable of having a value corresponding to the water content in the sample (only one water molecule is shown in Fig. 8).

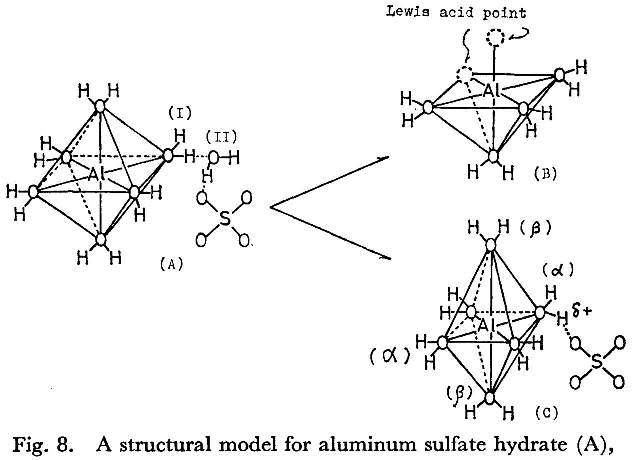

Fig. 8. A structural model for aluminum sulfate hydrate (A), the dehydrated aluminum sulfate hydrate (B) and the compressed aluminum sulfate hydrate (C).

Appearance of Lewis Acid at Higher Temperature. The proposed structural model explains the fact that Lewis acid appeared when the sample was heated to a temperature higher than 90°C. According to the results of the DTA and TGA experiments, the heating of the sample to a temperature higher than 90°C resulted in a considerable dehydration. Further, the total amount of the dehydration occurring at 90—104°C was found to be $\sim$12 mol-H_2O/mol-$Al_2(SO_4)_3$. This means that the coordinated water (I) was removed by the heating. If any of the coordinated water is removed, vacant sites may appear around an aluminum ion (Fig. 8(B)). These vacant sites may exhibit the nature of Lewis acid.

Acidity Change on Compression. A distorted structural unit shown in Fig. 8 (C) was considered to explain the appearance of a protonic acid center in the compressed sample. As can be seen in this figure, the octahedron around an aluminum ion is deformed. That is, the distance between the central Al^{3+} ion and each of the coordinated-water is no longer equivalent, and there appear two sorts of coordinated water, *i.e.*, H_2O (α) and $H_2O(\beta)$. Now, since the distance between Al^{3+} and $H_2O(\alpha)$ is smaller than the original value, stronger interaction between Al^{3+} and $H_2O(\alpha)$ may result and the covalent character in the Al^{3+}–$H_2O(\alpha)$ may increase. Thus, some positive charges may appear on the H atom in the $H_2O(\alpha)$ molecule. This is a protonic acid center. In this manner, the increased acidity of the compressed sample can be explained by considering the increased content of the distorted structural unit.

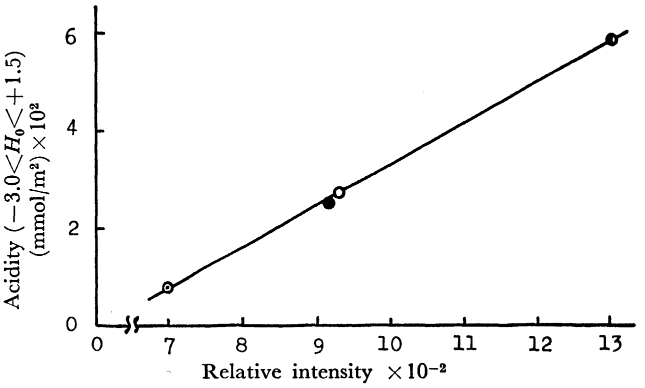

Fig. 9. Relations between the surface acidity ($H_0 = -3.0$—$+1.5$) and the relative intensity of the Raman ν_1 line for SO_4^{-2}: (◉) $P_{20,0}$; (◑) $P_{20,4200}$; (○) $P_{65,0}$; (●) $P_{65,4200}$.

In deforming the octahedral structural unit, chemical forces exerted by sulfate ions around the octahedron seem to play an important role. Since the compression results in the dehydration of anion-water (II), the sulfate ion may be displaced toward the octahedron. Therefore, the interaction between the sulfate ion and the coordinated water (α) may increase. This may promote the ionization of a H atom into $H^{\delta+}$ in the $H_2O(\alpha)$ molecule and result in the deformation of the octahedron. The experimental results shown in Fig. 9 indicate that, irrespective of the compacting pressure as well as the compacting temperature, the surface acidity of the sample can be regarded as a unique function of the relative intensity of the Raman ν_1 line of the sulfate ion. This fact indicates the intimate relation between the surface acidity and the behavior of sulfate ions in the sample.

Experimental Evidence for the Proposed Mechanism. The following experimental results also support the above described mechanism for the acidity change due to compression:

i) The existence of two kinds of coordinated water (α,β) in the compressed sample is supported by the following facts: (a) The DTA endothermic peak which corresponds to the dehydration of the coordinated water (II) was found to be a single peak for the uncompressed sample, whereas the peak for the compressed sample split into two peaks. (b) The far-in-

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9) D. Taylor and H. Basset, *J. Chem. Soc.*, **1952**, 4431.

frared spectra assigned to the O–Al–O deformation in the uncompressed sample appeared at 155 cm^{-1} as a single band, whereas the O–Al–O deformation absorption for the compressed sample split into two bands.

ii) One experimental fact (i-b) mentioned above supports the supposition that the degree of the interaction between the O atom and the Al^{3+} ion in a $H_2O(\alpha)$-Al^{3+}-$H_2O(\alpha)$ group may be different from that in a $H_2O(\beta)$-Al^{3+}-$H_2O(\beta)$ group.

iii) The supposition that the interaction between the sulfate ion and the H atom in a $H_2O(\alpha)$ molecule would be increased by compression may be supported by the fact that the infrared absorption which was assigned to the O–H stretching vibration shifted toward a somewhat lower wave number as the compacting pressure of the sample was increased.

iv) The displacement of sulfate ions toward an octahedron may result in an increase in the concentration of the sulfate ion in the sample. This expectation was supported by the fact that the relative intensity of the Raman ν_1 peak of the sulfate ion increased on the compression of the sample.