

ferrites.²⁶ Therefore, the contribution of the $B-B$ interaction to the uniaxial energy will be small. Furthermore, the $B-B'$ interaction is collinear through the intermediate oxygen ion. Since this satisfies the condition for strongest coupling, the $B-B$ interaction can

²⁶ E. W. Gorter, Philips Research Repts. 9, 295, 321, 403 (1954).

be neglected compared with the $B-B'$. Thus, of the four types of interactions which occur in ferrites with cation excess, our model predicts that only the $B-B'$ interaction can give rise to a sizeable annealing effect. This predicted effect is in accord with our experimental results.

Dielectric and Thermal Study of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$ Transitions*

S. HOSHINO, K. VEDAM, Y. OKAYA, AND R. PEPINSKY

Department of Physics, The Pennsylvania State University, University Park, Pennsylvania

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The behavior of the various dielectric properties, specific heat, and thermal expansion of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$ has been studied in detail under various experimental conditions, with particular reference to the ferroelectric transitions in these crystals. The curves of dielectric constant *vs* temperature do not obey the Curie-Weiss law. The shift of the transition temperature as reported in the literature could not be detected even under extreme experimental conditions. The transition energy and entropy change have been evaluated from a C_p *vs* T curve. The variation of the lattice parameters and the unit cell volumes with temperature has been measured by the x-ray method.

The transition of $(\text{NH}_4)_2\text{SO}_4$ appears to be of first order, while that of $(\text{NH}_4)_2\text{BeF}_4$ is also of first but very close to second-order. Deuteration of these crystals does not affect the transition of $(\text{NH}_4)_2\text{SO}_4$; but in the case of $(\text{NH}_4)_2\text{BeF}_4$ the transition temperature is raised by 3°C by deuteration, and the transition energy is also increased.

The phase diagram of $(\text{NH}_4)_2\text{SO}_4$ — $(\text{NH}_4)_2\text{BeF}_4$ system is given.

INTRODUCTION

IT is well known that ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ has a phase transition at -50°C . The measurement of the various physical properties connected with this transition has been the subject of study by numerous investigators¹⁻¹⁰; but only recently Matthias and Remeika¹¹ discovered that this crystal becomes ferroelectric below the transition point. No detailed investigation on the dielectric properties of this crystal with particular reference to the ferroelectric transition has been carried out so far. The only observations reported in the literature are those of Kamiyoshi¹² and Le Montagner,¹³ both of whom carried out measurements

on the dielectric constant under various experimental conditions. Kamiyoshi found an unbelievably large shift of the transition temperature by the application of a dc electric field. Le Montagner reported that the transition temperature of $(\text{NH}_4)_2\text{SO}_4$ is shifted to -38°C by carrying out the measurements in vacuum.

Ammonium fluoberyllate, $(\text{NH}_4)_2\text{BeF}_4$, has a transition at -97°C , and Pepinsky and Jona¹⁴ found that the low-temperature phase of this crystal was also ferroelectric. No detailed study on the phase transition has been reported as yet. The crystal structure of $(\text{NH}_4)_2\text{BeF}_4$ at room temperature was reported as isomorphous with $(\text{NH}_4)_2\text{SO}_4$.^{15,16} The fact that these crystals are actually nonisomorphous was discovered by Okaya *et al.*¹⁷ by a precise x-ray study. It was found that the symmetries of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$ differ from one another in both their room-temperature and low-temperature phases; and, furthermore, the polar axes in the ferroelectric phases of these two crystals are not in the same crystallographic direction. One can expect, therefore, that the nature of the phase transition of $(\text{NH}_4)_2\text{BeF}_4$ is different from that of $(\text{NH}_4)_2\text{SO}_4$.

The facts described above suggest the necessity of

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¹ G. Hettner and F. Simon, *Z. physik. Chem.* **B1**, 293 (1928).

² J. L. Grenshaw and I. Ritter, *Z. physik. Chem.* **B16**, 143 (1932).

³ C. H. Shomate, *J. Am. Chem. Soc.* **67**, 1096 (1945).

⁴ I. Nitta and K. Suenaga, *Bull. Chem. Soc. Japan* **13**, 36 (1938).

⁵ A. Hettich, *Z. physik. Chem.* **A168**, 360 (1934).

⁶ R. Guillion, *Compt. rend.* **208**, 980 (1939); *Ann. phys.* **17**, 334 (1942).

⁷ S. T. Bayley, *Trans. Faraday Soc.* **47**, 518 (1951).

⁸ M. Freymann, *Compt. rend.* **233**, 1449 (1951).

⁹ Freymann, Rolland, and Freymann, *Compt. rend.* **232**, 2312 (1951).

¹⁰ R. Pohlman, *Z. Physik* **79**, 344 (1932).

¹¹ B. T. Matthias and J. P. Remeika, *Phys. Rev.* **103**, 262 (1956).

¹² K. Kamiyoshi, *Science Repts. Research Insts. Tôhoku Univ.* **A9**, 94 (1957); *J. Chem. Phys.* **26**, 218 (1957).

¹³ S. Le Montagner, thesis, University of Paris, 1957 (unpublished).

¹⁴ R. Pepinsky and F. Jona, *Phys. Rev.* **105**, 344 (1957).

¹⁵ P. L. Mukherjee, *Indian J. Phys.* **18**, 148 (1944).

¹⁶ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1953), Vol. II, Chap. 8, p. 47.

¹⁷ Okaya, Vedam and Pepinsky, *Acta Cryst.* **11**, 307 (1958).

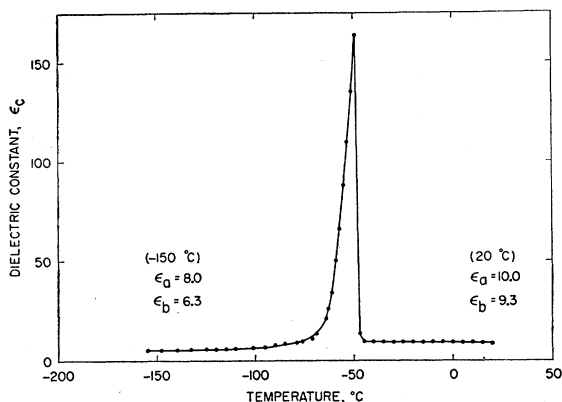


FIG. 1. $(\text{NH}_4)_2\text{SO}_4$: Dielectric constant vs temperature

re-examination of the physical properties of $(\text{NH}_4)_2\text{SO}_4$, and the carrying out of a similar detailed study of $(\text{NH}_4)_2\text{BeF}_4$, in order to understand the mechanism of the ferroelectric phase transitions in both crystals. The results obtained on the measurements of the dielectric properties, specific heat and thermal expansion of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$ and their solid solutions, as well as the corresponding deuterated samples, are described below.

In what follows, the accepted modern convention for the notation of the crystallographic axes is adopted; i.e., $c < a < b$. Thus for $(\text{NH}_4)_2\text{SO}_4$, one has¹⁶ $a = 7.729$ Å, $b = 10.560$ Å, and $c = 5.951$ Å; and for the "basic cell"¹⁷ of $(\text{NH}_4)_2\text{BeF}_4$, one has¹⁵ $a = 7.49$ Å, $b = 10.39$ Å, and $c = 5.89$ Å at room temperature.

DIELECTRIC MEASUREMENTS

The low-temperature behavior of the dielectric constant ϵ_c of $(\text{NH}_4)_2\text{SO}_4$ at a frequency of 10 kc/sec and a field of 5 v/cm is represented in Fig. 1, as a function of temperature. The dielectric constant ϵ_c has a value of about 9.2 at room temperature, and this value remains constant until the phase transition temperature at -49.5°C is nearly reached. The dielectric constant

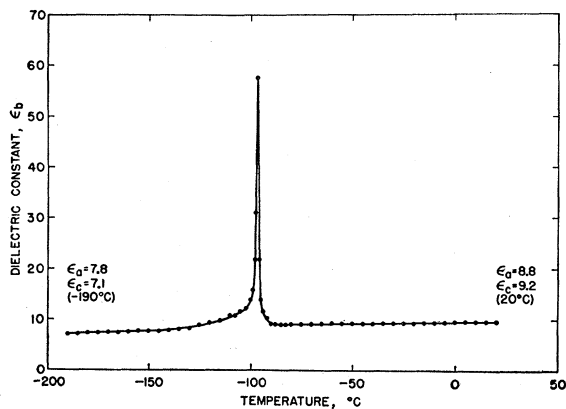


FIG. 2. $(\text{NH}_4)_2\text{BeF}_4$: Dielectric constant vs temperature.

suddenly jumps to a high value of 165 at -49.5°C . As the temperature is further lowered, this value drops to nearly the original value at about -65°C . The rate of cooling or warming of the crystal affects the shape of the curve, in that the slower the rate of cooling, the sharper the peak; and the temperature range over which the dielectric constant has a large value is also lowered. In the present experiments the rate of cooling near the transition temperature was 1°C in 4 minutes.

A fairly similar behavior is noticed for the case of $(\text{NH}_4)_2\text{BeF}_4$, under identical experimental conditions. Figure 2 represents the variation of ϵ_b of $(\text{NH}_4)_2\text{BeF}_4$ with temperature. In both $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$

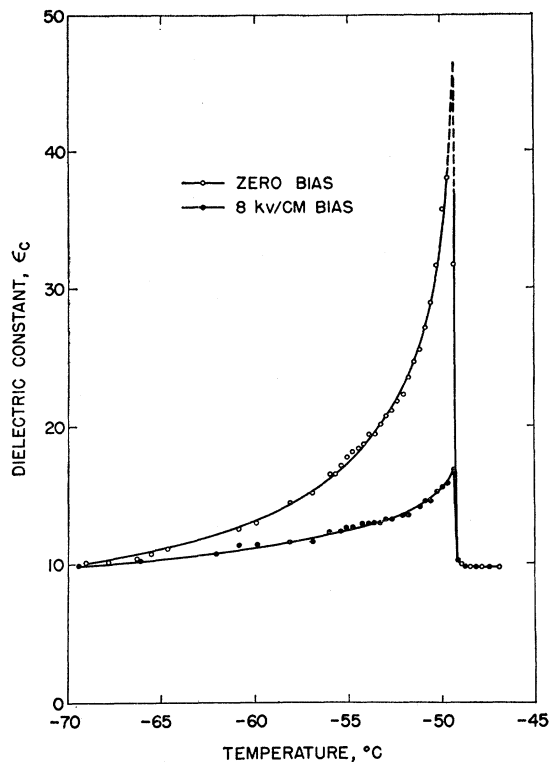


FIG. 3. $(\text{NH}_4)_2\text{SO}_4$: Effect of dc biasing field on dielectric constant, ϵ_c .

no dielectric anomaly was noticed at the transition temperature when the electric field was applied along the other two crystallographic directions, namely, a and b for $(\text{NH}_4)_2\text{SO}_4$, and a and c for $(\text{NH}_4)_2\text{BeF}_4$. For these directions the dielectric constant merely progressively decreases slightly as the temperature is lowered. The numerical values at room temperature and at a temperature near that of liquid nitrogen are also entered in Figs. 1 and 2.

A small but reproducible thermal hysteresis of 1°C was noticed in the case of $(\text{NH}_4)_2\text{SO}_4$, on comparing the transition temperatures during warming and cooling. On the other hand, in $(\text{NH}_4)_2\text{BeF}_4$ the thermal hysteresis, if it exists at all, is not more than 0.5°C .

At this point, mention may be made of the results obtained by Le Montagner¹³ on the effect of vacuum on the transition temperature of $(\text{NH}_4)_2\text{SO}_4$. According to Le Montagner, the transition temperature can be shifted to higher temperatures (about -38°C) when the measurements on the crystal are carried out in vacuum; and this result was explained by him as due to the effect of an adsorbed layer of water on the crystal. In one of our own experiments a crystal of $(\text{NH}_4)_2\text{SO}_4$ was kept in vacuum at a pressure of 1×10^{-5} mm Hg for two days, and then was very rapidly transferred to a medium of dry nitrogen, in which the dielectric measurements were carried out. The transition tempera-

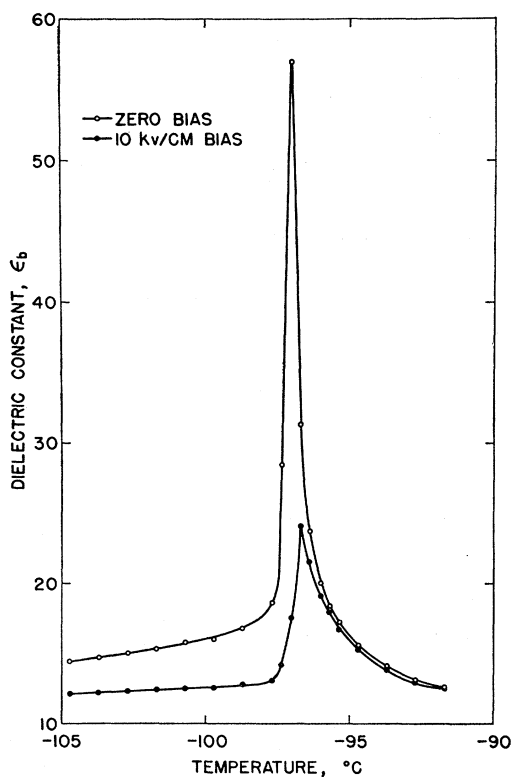


FIG. 4. $(\text{NH}_4)_2\text{BeF}_4$: Effect of dc biasing field on dielectric constant, ϵ_b .

ture recorded under these conditions did not vary from our previously measured values within the limits of experimental error.

According to Kamiyoshi,¹² the transition in $(\text{NH}_4)_2\text{SO}_4$ can either be "suppressed or accelerated" by the application of a dc electric field. According to him the transition temperature can be shifted to as low a temperature as -82°C , or can even be raised to as high a temperature as -15°C . No such shift in the transition temperature of $(\text{NH}_4)_2\text{SO}_4$ could be observed by us, even with an applied electric field of 30 kv/cm. Further, according to Kamiyoshi, the value of the dielectric constant increases at any temperature by the application

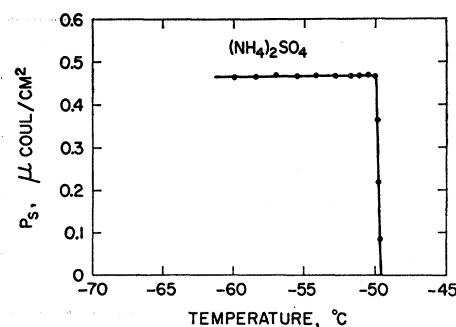


FIG. 5. $(\text{NH}_4)_2\text{SO}_4$: Spontaneous polarization vs temperature in the neighborhood of the Curie point.

or reversal of the electric field. Again no such phenomenon was observed, as the accompanying Fig. 3 shows. Here the experimental arrangement was such that one could apply or reverse the polarity, or remove the dc field suddenly, by throwing a switch, and the dielectric constant could be measured at each setting. Similar measurements carried out on various single crystals and pressed powder samples, with different prehistories such as (1) untreated, (2) annealed at 80°C for ten days, (3) evaporated or painted electrodes, etc., did not alter the above conclusions. Figure 4 represents the results of similar measurements on the field-dependence of the transition temperature and the dielectric constant of $(\text{NH}_4)_2\text{BeF}_4$.

Figures 5 and 6 show the variation of the spontaneous polarization with temperature of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$, respectively. Immediately above the transition temperature in $(\text{NH}_4)_2\text{BeF}_4$ one can clearly observe the well-known double hysteresis loops of the type observed by Merz¹⁸ in the case of BaTiO_3 . However, no such loops could be detected in $(\text{NH}_4)_2\text{SO}_4$ even with an applied field of 30 kv/cm, and with very slow variation of temperature near the transition point.

Figures 7 and 8 represent the variation of the coercive field of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$, respectively, in the vicinity of the transition temperatures.

The transition in $(\text{NH}_4)_2\text{SO}_4$ is rather violent, so that

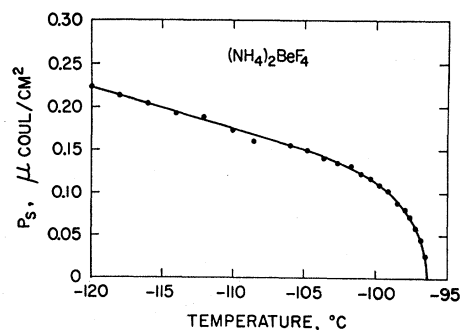


FIG. 6. $(\text{NH}_4)_2\text{BeF}_4$: Spontaneous polarization vs temperature in the neighborhood of the Curie point.

¹⁸ W. J. Merz, Phys. Rev. 91, 513 (1953).

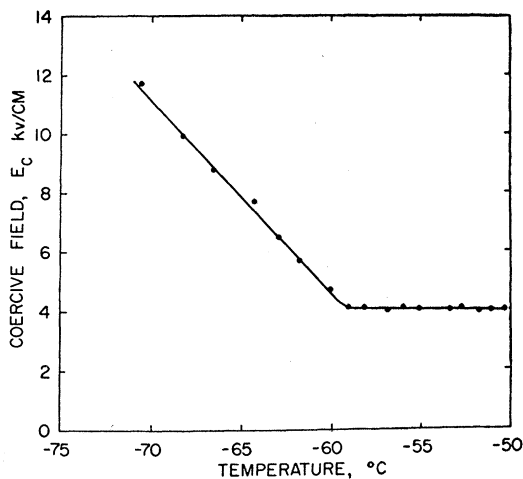


FIG. 7. $(\text{NH}_4)_2\text{SO}_4$: Coercive field *vs* temperature.

the crystal usually shatters to bits when it is taken through the transition, unless the sample is fairly thin and the rate of variation of the temperature is very slow. No such behavior was noticed in the case of $(\text{NH}_4)_2\text{BeF}_4$.

EFFECT OF DEUTERATION

Deuterated samples of these salts, $(\text{ND}_4)_2\text{SO}_4$ and $(\text{ND}_4)_2\text{BeF}_4$, were obtained by recrystallizing from a solution of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$, respectively in 99.9% D_2O . The dielectric behavior of $(\text{ND}_4)_2\text{SO}_4$ was found to be exactly the same as that of $(\text{NH}_4)_2\text{SO}_4$, within the limits of experimental errors. On the other hand, $(\text{ND}_4)_2\text{BeF}_4$ was found to have a transition temperature 3° higher than that of $(\text{NH}_4)_2\text{BeF}_4$. Otherwise the shape of the ϵ *vs* T curve and the values of P_s , etc., was quite the same within the limits of experimental error.

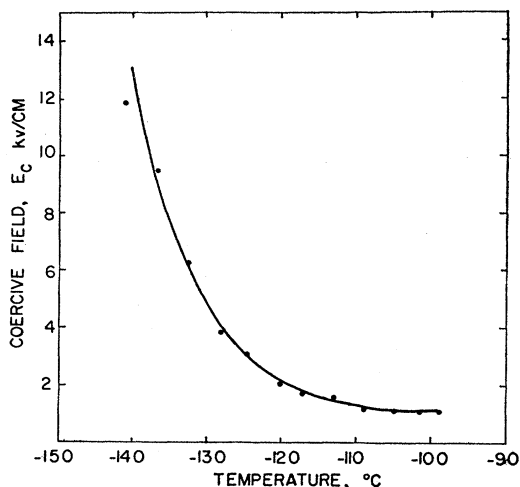


FIG. 8. $(\text{NH}_4)_2\text{BeF}_4$: Coercive field *vs* temperature.

SPECIFIC HEAT MEASUREMENTS

The apparatus used in the present work was an adiabatic calorimeter of the modified Sykes' type.¹⁹ This calorimeter was altered to permit low- as well as high-temperature measurements. The outer tube was shielded by Styrofoam, and the liquid nitrogen vessel was placed on the lid of the outside heater. As a result of these modifications we can now measure specific heats in the temperature range from -140°C to $+650^\circ\text{C}$.

The sample is enclosed in a vessel made of thin paper (about 0.1 g). About ten grams of sample are used in the measurements. The heat input to the sample is between 0.001 and 0.002 cal/g sec. The heating rate resulting is in the range from 0.7 to 0.3 degree/min in the normal part of the specific heat range.

THERMAL RESULTS FOR $(\text{NH}_4)_2\text{SO}_4$

The specific heat anomaly of $(\text{NH}_4)_2\text{SO}_4$ has been reported by Shomate,³ and by Nitta and Suenaga⁴ who found a typical lambda-type anomaly at -50°C . Al-

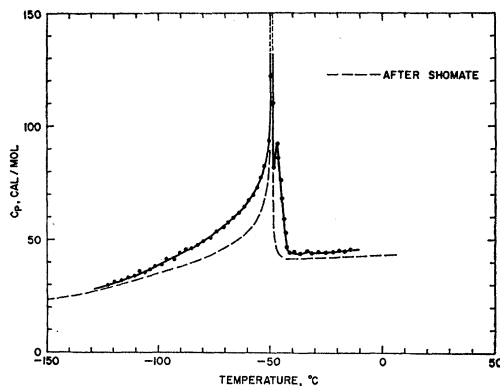


FIG. 9. $(\text{NH}_4)_2\text{SO}_4$: Specific heat *vs* temperature.

though the shift of the transition temperature as reported in the literature^{12,13} was not found by the dielectric measurement by us, it seemed desirable to perform the specific heat measurements using very pure samples under various conditions: (1) cp (Baker) powder sample, no heat treatment; (2) same material, preheated at 75°C for ten days; (3) same material, preheated up to 175°C ; (4) same material, ground severely; (5) pulverized sample from good single crystals, without any heat treatment; (6) same material as (5), preheated up to 120°C .

The results obtained in every case are exactly the same within the limits of experimental error. The specific heat *vs* temperature curve in the vicinity of the transition is shown in Fig. 9. Anomalies are observed at two temperatures: one at -50°C , coinciding with the Curie point, and another at -47.5°C . Even though the measurements are extended on either side, i.e., from -130°C

¹⁹ S. Nagasaki and Y. Takagi, J. Appl. Phys. (Japan) 17, 104 (1948).

to +170°C, no other anomaly was detected. The estimated transition energy ΔQ and the entropy change ΔS of the double peak do not differ among the six samples investigated, and have the following values:

$$\Delta Q = 0.93 \text{ kcal/mole}; \quad \Delta S = 4.2 \text{ cal/mole deg.}$$

These values are in good agreement with Shomate's data.³

THERMAL RESULTS FOR (ND₄)₂SO₄

Here again two peaks were observed in the specific heat curve, at -49.5°C and -48.0°C, as shown in Fig. 10. Within the limits of experimental error, the entropy change ΔS was the same as found for (NH₄)₂SO₄.

THERMAL RESULTS FOR (NH₄)₂BeF₄

Measurements were performed on the following materials: (1) powder sample pulverized from large single crystals, without any heat treatment; (2) same material as (1), but preheated at 75°C for 8 days.

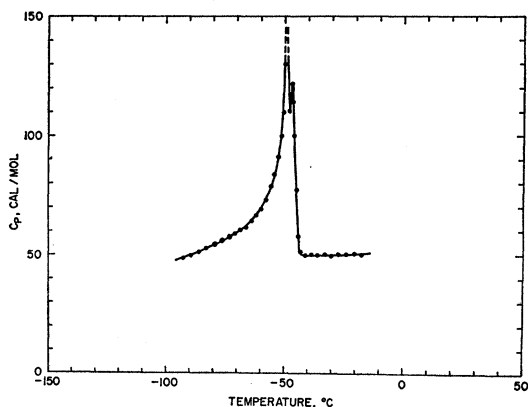


FIG. 10. (ND₄)₂SO₄: Specific heat vs temperature.

The specific heat curves for these two samples are almost the same. The measurement was carried out from -140°C to +130°C, and only one anomaly was found at the ferroelectric transition temperature. Figure 11 represents the specific heat vs temperature curve of (NH₄)₂BeF₄. The transition energy ΔQ and entropy change ΔS are estimated as:

$$\Delta Q = 0.31 \text{ kcal/mole}; \quad \Delta S = 1.90 \text{ cal/mole deg.}$$

THERMAL RESULTS FOR (ND₄)₂BeF₄

The same type of specific heat anomaly as (NH₄)₂BeF₄ was obtained (Fig. 12) for the deuterated material, but the transition temperature is slightly higher than that of (NH₄)₂BeF₄, in conformity with our dielectric measurements. The transition energy ΔQ and the estimated entropy change ΔS are larger than those of (NH₄)₂BeF₄, and have the following values:

$$\Delta Q = 0.38 \text{ kcal/mole}; \quad \Delta S = 2.27 \text{ cal/mole deg.}$$

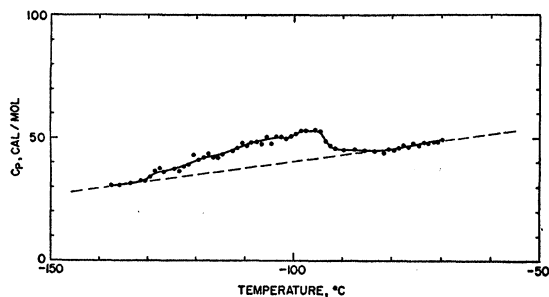


FIG. 11. (NH₄)₂BeF₄: Specific heat vs temperature.

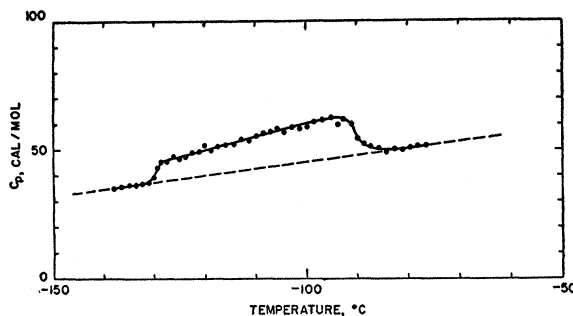


FIG. 12. (ND₄)₂BeF₄: Specific heat vs temperature.

THERMAL EXPANSION MEASUREMENTS

Observations of thermal expansions of (NH₄)₂SO₄ and (NH₄)₂BeF₄ were made by precise x-ray measurement of changes of lattice constants with temperature. A low-temperature x-ray camera of 114.6-mm diameter was used, with Cu K α radiation. The single-crystal back-reflection technique was employed in these investigations. Figures 13 and 14 represent the variation of the

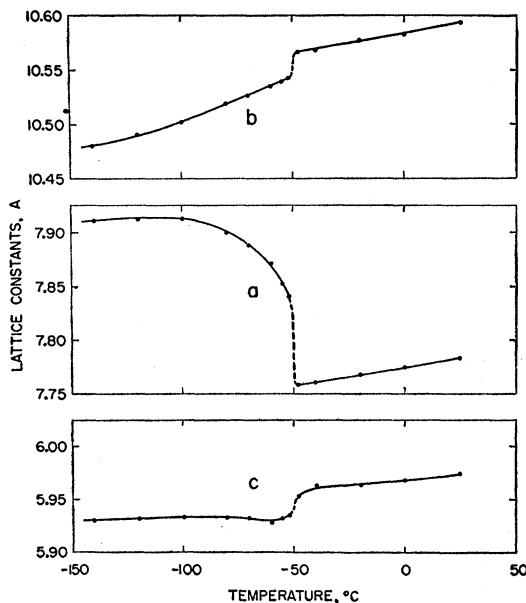


FIG. 13. (NH₄)₂SO₄: Lattice constants vs temperature.

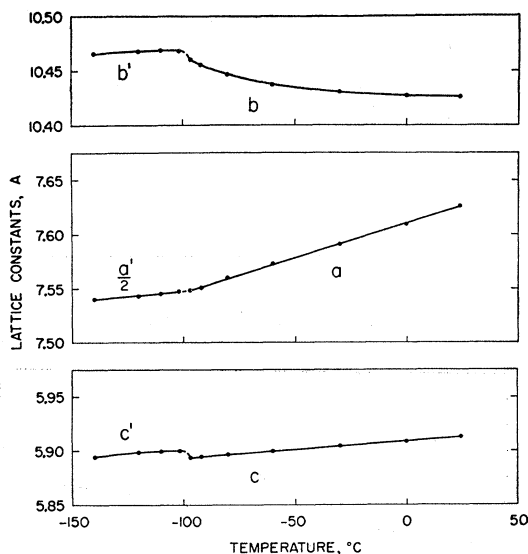


FIG. 14. $(\text{NH}_4)_2\text{BeF}_4$: Lattice constants vs temperature.

lattice constants of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$, respectively with temperature. According to Okaya *et al.*,¹⁷ $(\text{NH}_4)_2\text{BeF}_4$ exhibits superstructure along the b and c axes at room temperature, the true cell dimensions being a , $2b$, and $2c$. Below the transition point, the a axis is also doubled. In other words, the "basic cell" of the low-temperature phase is $a' \cong 2a$, $b' \cong b$, and $c' \cong c$; and the true cell is $a'' = a'$, $b'' = 2b'$, and $c'' = 2c'$.

On the other hand, in the case of $(\text{NH}_4)_2\text{SO}_4$ the superstructure was observed along the b and c axes at room temperature in a few cases, but not always; and in no case was a -axis doubling observed in the low-temperature phase. In the figures, the variation of lattice parameters of the "basic cell" is illustrated.

Figure 15 shows the unit cell volume as a function of temperature.

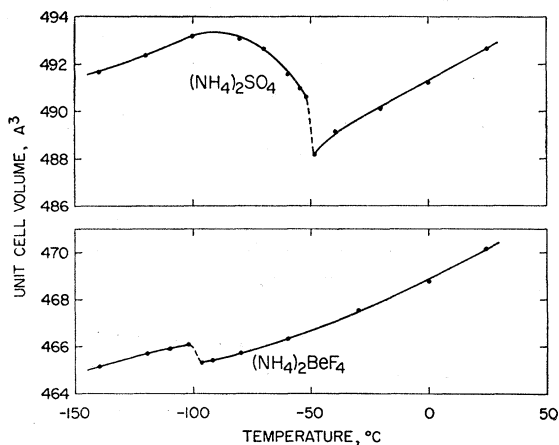


FIG. 15. Unit cell volume vs temperature curve of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$.

PHASE DIAGRAM OF $(\text{NH}_4)_2\text{SO}_4 - (\text{NH}_4)_2\text{BeF}_4$ SYSTEM

Single crystals of various concentrations of the solid solutions of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$ were grown from aqueous solutions. The composition for each crystal was estimated from the density values, determined by the flotation method. The dielectric constant vs temperature curve was obtained for each concentration to detect the transition temperature, and x-ray photographs were taken for determination of the lattice symmetry and space group. From these results the phase diagram of $(\text{NH}_4)_2\text{SO}_4 - (\text{NH}_4)_2\text{BeF}_4$ system was drawn as shown in Fig. 16.

As seen in the diagram, for intermediate compositions ranging from about 20 to 70 mole % of $(\text{NH}_4)_2\text{BeF}_4$ no

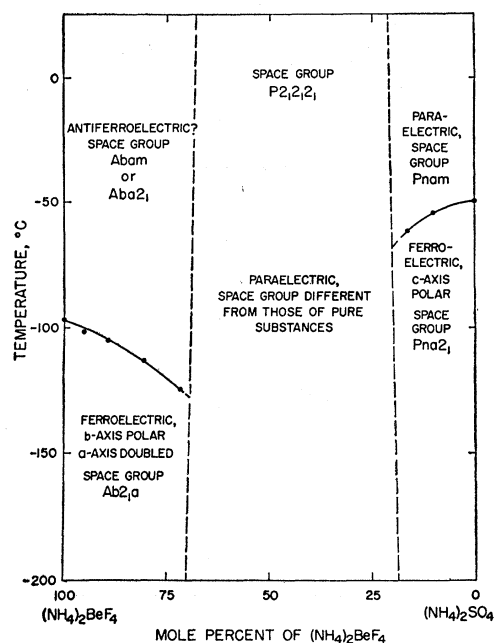


FIG. 16. Phase diagram of $(\text{NH}_4)_2\text{BeF}_4 - (\text{NH}_4)_2\text{SO}_4$ system.

transition could be detected in the temperature range $+25^\circ\text{C}$ to -196°C . The space group for these compositions was found to be $P2_12_12_1$ at room temperature.

DISCUSSION

Before proceeding to discuss the results obtained, it would be worth while to again point out that we could not detect any noticeable shift of the transition temperatures of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$ either by reducing the working pressure, by the application of a dc electric field, or even by exposing the experimental sample to extreme conditions. In these respects our results disagree with those obtained by Kamiyoshi¹² and by Le Montagner.¹³

One of the striking features noticed in these studies is the fact that the shape of the ϵ vs T curves of $(\text{NH}_4)_2\text{SO}_4$

and (NH₄)₂BeF₄ is rather unusual for a ferroelectric transition. The Curie-Weiss law is not obeyed above the transition temperature, unlike most of the ferroelectrics discovered thus far. The only other examples are: (NH₄)₂Cd₂(SO₄)₃,²⁰ which has a dielectric behavior almost similar to that of the present crystals; and NaNH₄ tartrate,²¹ which undergoes a phase transition with just a small but abrupt decrease of the dielectric constant.

At this point mention may be made of the measurements of Couture, Le Montagner, *et al.*²² and Freymann⁸ on the dielectric behavior of (NH₄)₂SO₄ at microwave frequencies. These authors found a normal type of dielectric behavior at the high frequencies. In other words, the dielectric behavior of the crystal seems to undergo a radical change at some frequency between 10 kc/sec and 24 000 Mc/sec. In order to understand this phenomenon, measurements on the dielectric properties were carried out by us at a number of frequencies between 10 kc/sec and 50 Mc/sec, using a Boonton *Q* meter. It was found that the lower limit of the frequencies at which (NH₄)₂SO₄ exhibits a normal type of dielectric behavior occurs in the megacycle region, the actual value of the frequency depending on the thickness of the crystal. This indicates that when one is measuring at very high frequencies, he is actually measuring the clamped dielectric constant, while at low frequencies the measured value yields the free dielectric constant. Hence it is not surprising to find noticeable differences in the shape of the ϵ vs *T* curves of (NH₄)₂SO₄ at different frequencies.

As mentioned earlier, the rate of cooling or warming of the crystal near the transition temperature affects the shape of the low-frequency dielectric constant vs temperature curve considerably. It was found that the slower the rate of variation of temperature, the sharper is the peak, and the temperature range over which the dielectric constant has a large value is also narrowed. Very recently Makita and Takagi²³ have found that with an extremely slow rate of variation of temperature (about 1°C in 14 minutes), (NH₄)₂SO₄ exhibits a normal type of dielectric behavior.

The value of the spontaneous polarization of (NH₄)₂SO₄ given in Fig. 3 represents the highest values obtained by the authors from among several crystals. Since the values fluctuated by as much as 50% from one to another, one might conjecture that a single-domain crystal is not usually obtained, and that in a multidomain crystal some of the domains are clamped so that they cannot reverse their polarities.

The specific heat vs temperature curves for (NH₄)₂SO₄ and (NH₄)₂BeF₄ indicate that the mechanisms of the phase transitions of these two crystals are of different

type. There seems to be evidence of the appearance of latent heat in the (NH₄)₂SO₄ transition, whereas (NH₄)₂BeF₄ exhibits a broad peak at the transition, similar to that observed in the ferroelectric transition of (glycine)₃·H₂SO₄,²⁴ at 47°C which is presumed to be a typical second-order transition.

Furthermore, the specific heat data of (NH₄)₂SO₄ provide some interesting features. As mentioned before, two peaks are observed in the *C_p* vs *T* curve: one at -50°C and the other at -47.5°C, irrespective of the prehistory of the sample. A critical analysis of the results obtained in the various runs seems to indicate that the rate of variation of temperature affects the temperature of the second peak, whereas the peak at -50°C is not affected. It appears that the slower the rate of variation of temperature, the less is the temperature difference between the two peaks. Thus it is quite probable that one might obtain only one peak at -50°C, with an extremely slow rate of variation of temperature. This is possibly the reason why Shomate³ and Nitta and Suenaga⁴ obtained only one peak in their measurements. Again, one is tempted to relate this phenomenon with the radical change noticed in the dielectric behavior of this crystal with different rates of cooling or warming. In other words, these data indicate the existence of a relaxation mechanism with very large relaxation time.

As seen in Figs. 13 and 14, the variations of the lattice constants of (NH₄)₂SO₄ and (NH₄)₂BeF₄ through their transition points are the opposite of each other along any corresponding axis, and the variation for (NH₄)₂SO₄ is much more drastic than that for (NH₄)₂BeF₄. These facts again suggest differences in the transition mechanisms of these two crystals. In both (NH₄)₂SO₄ and (NH₄)₂BeF₄, it is seen from Fig. 15 that as the temperature is increased the unit cell volume undergoes a contraction at the transition point. This is in agreement with the results of dilatometric measurement by Nitta and Suenaga.⁴

Even a casual survey of the results described above immediately leads us to the conclusion that the transition in (NH₄)₂SO₄ is of first order. Some of the factors leading to the above conclusion are: the abrupt discontinuity in *P_s* vs *T* curve; the appearance of latent heat at the transition; the very large and abrupt variation of the lattice dimensions of the crystal—and hence the strain with consequent shattering of the crystal—during the transition; etc. The absence of the double hysteresis loops in a transition of this kind is rather unique here; generally, ferroelectric crystals which have a first-order transition do exhibit double hysteresis loops at temperatures just above the transition temperature. The reason for this is not far to seek, if one evaluates the variation of transition temperature with the applied field from the formula $\partial T_c / \partial E = -\Delta P / \Delta S$. On substitution of the indicated values one finds, for a field of 20 kv/cm, a

²⁰ F. Jona and R. Pepinsky, *Phys. Rev.* **103**, 1126 (1956).

²¹ Y. Takagi and Y. Makita, *J. Phys. Soc. Japan* **13**, 272 (1958).

²² Couture, Le Montagner, Le Bot, and Le Traon, *Compt. rend.* **242**, 1804 (1956).

²³ Y. Makita and Y. Takagi, private communication.

²⁴ Hoshino, Mitsui, Jona, and Pepinsky, *Phys. Rev.* **107**, 1255 (1957).

shift of the transition temperature of only 0.05°C , and hence it is not surprising that no shift of the Curie temperature is detected in the dielectric measurement (Fig. 2), and that the double hysteresis loops fail to appear.

On the other hand, the situation in $(\text{NH}_4)_2\text{BeF}_4$ is quite the opposite. Above the transition temperature one definitely observes double hysteresis loops, thereby clearly demonstrating that the transition is of first order. However, when one considers the smooth change of P_s with temperature at the transition point, the shape of the specific heat curve, and the thermal expansion data, the transition could be considered as of second order.

X-ray studies on $(\text{NH}_4)_2\text{BeF}_4$ provide an interesting clue to this peculiar behavior. As mentioned before, superstructuring has been observed along the b and c axes at room temperature. And as the crystal is cooled below the transition point, one finds the a axis in addition is doubled. Thus the question arises: whether $(\text{NH}_4)_2\text{BeF}_4$ is antiferroelectric at room temperature and the transition at -97°C is from an antiferroelectric state to a *ferrielectric* state. Here the word *ferrielectric* is used according to the terminology of Cross²⁵ and Känzig.²⁶ Detailed structure analyses by x-ray and neutron diffraction methods, in progress here and at Brookhaven National Laboratory, should provide an answer to this puzzle. However, on the assumption that $(\text{NH}_4)_2\text{BeF}_4$ is antiferroelectric at room temperature, one can expect another transition at high tem-

perature, the crystal transforming from an antiferroelectric to a paraelectric state. To test this possibility, dielectric measurements were carried out at high temperatures up to the decomposition point. Except for a slight apparent increase in the value of the dielectric constant at very high temperature, due to an increase in conductivity, no noticeable anomaly was observed in any of the three crystallographic directions up to 225°C , where the crystal decomposes. A phase transition might exist at higher temperature, but this temperature is higher than the decomposition point. Thus only a complete structure analysis of $(\text{NH}_4)_2\text{BeF}_4$ can establish whether the crystal is paraelectric or antiferroelectric at room temperature.

Several points do establish the fact that the mechanism of transition in $(\text{NH}_4)_2\text{BeF}_4$ is quite different from that of $(\text{NH}_4)_2\text{SO}_4$. Furthermore, from the fact that the deuteration of $(\text{NH}_4)_2\text{SO}_4$ does not affect the transition temperature one might conjecture that the transition may not depend only on the order-disorder arrangement of NH_4^+ radicals, just as in the case of NH_4Cl . The same cannot be said of $(\text{NH}_4)_2\text{BeF}_4$, since deuteration in this case shifts the transition point by 3°C .

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²⁵ L. E. Cross, *Phil. Mag.* (8) 1, 76 (1956).

²⁶ W. Känzig, *Solid State Physics* (Academic Press, Inc., New York, 1957), p. 8.