explained, even qualitatively, by any current theory of thermoelectricity.

The Lorenz number for high-purity copper has approximately the same temperature behavior as has been observed by others previously.[17,19] However, the curve does not seem to extrapolate to the Sommerfeld value at 0°K, but rather flattens out to a considerably lower value. The same phenomenon has been observed in two very dilute copper alloys.

VI. ACKNOWLEDGMENTS

We would like to thank Dr. R. H. Sherman of the Los Alamos Scientific Laboratory for assistance in the preparation of the samples and Dr. A. J. Phillips and J. S. Smart, Jr., of the Central Research Laboratories of the American Smelting and Refining Company for supplying the original high-purity rods. We would also like to thank M. D. Bunch and M. Konecnik for assistance during many of the experimental runs.

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Crystal Structure of the Ferroelectric Phase of $(\text{Glycine})_3\cdot H_2SO_4$†

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Ferroelectric $(\text{glycine})_3\cdot H_2SO_4$ crystallizes at room temperature in the monoclinic system with $a=9.41_7$ A, $b=12.64_3$ A, $c=5.73_5$ A, $\beta=110°\ 23'$; the space group is $P2_1$, and the polar direction is along the two-fold screw axis. Above 47°C the spontaneous polarization disappears as the space group becomes $P2_1/m$. The crystal structure was determined from full three-dimensional x-ray diffraction data, using Cu $K\alpha$ radiation. Out of the three glycine molecules in the crystal, one has the usual zwitter-ion configuration, with the $-NH_3^+$ group out of the plane of the other atoms; the remaining two glycines are mono-protonated, and planar within experimental error, and are designated as glycinium ions. Thus the chemical formula is properly written as $(NH_3^+CH_2COO^-)\cdot(NH_3^+CH_2COOH)_2\cdot SO_4^{--}$, and the compound is best described by the chemical name glycine diglycinium sulfate. One of the planar glycinium ions lies near but not in the plane $y=\frac{1}{4}$, which becomes the mirror plane in the high-temperature phase.

The nitrogen atoms form $N-H\cdot\cdot O$ hydrogen bonds of the usual strength, whereas a quite strong $O-H\cdot\cdot O$ hydrogen bond of a distance of 2.43_8 A is found between the oxygen atom of the carboxyl group of the zwitter-ion glycine and that of the planar glycinium ion which lies near the plane $y=\frac{1}{2}$.

Above the Curie point, at 47°C, mirror symmetry is attained by statistical arrangement of atoms around the mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. The disorder of the glycinium ions near the mirror planes, and the above-mentioned strong $O-H\cdot\cdot O$ bond, are of particular importance for the ferroelectric behavior of the crystal.

INTRODUCTION

MATTHIAS, Miller, and Remeika[1] discovered ferroelectric behavior at room temperature in the crystals $(\text{glycine})_3\cdot H_2SO_4$ and isomorphous $(\text{glycine})_3$ H_2SeO_4. Pepinsky, Okaya, and Jona[2] later observed ferroelectricity in isomorphous $(\text{glycine})_3\cdot H_2BeF_4$. Preliminary x-ray and morphological studies of these crystals[2,3] revealed that the crystals belong to the space group $P2_1$ in their ferroelectric phase, changing into $P2_1/m$ above the Curie points; the transition temperatures are 47°C, 22°C, and 70°C for the sulfate, selenate, and fluoberyllate, respectively. Since detailed dielectric and thermal studies of the crystals[4] showed that the ferroelectric transition in these substances is of second order, the deviation of the structure from the centrosymmetric space group $P2_1/m$ to the ferroelectric phase could be presumed to be slight. Complete crystal structure analyses of both the polar and nonpolar phases of $(\text{glycine})_3\cdot H_2SO_4$, which is the most important ferroelectric among these isomorphs, are necessary in order to establish the nature of the hydrogen-bond system and also the configurations of the glycine and sulfate ions. Such a study is particularly important because discoveries within the last few years of a number of ferroelectric crystals suggest that hydrogen bonds in these crystals, and/or the presence of ions with particular symmetries—and especially those with tetrahedral, pyramidal, or planar configurations—play a dominant role in their dielectric behaviors.

These factors are suggested by a partial list of other newly-discovered ferroelectrics containing ammonium or substituted ammonium, glycine or guanidinium ions, and sulfate (or selenate or fluoberyllate), nitrate, or selenite ions. Included among these compounds are guanidinium$\cdot Al(SO_4)_2\cdot 6H_2O$ and isomorphs,[5] $(NH_4)_2$-

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† Research supported by contracts with the Air Force Office of Scientific Research (ARDC), the Signal Corps Engineering Laboratories, the U. S. Atomic Energy Commission, and by Brookhaven National Laboratory. Computations supported by contracts with the Office of Naval Research and by the U. S. Atomic Energy Commission.

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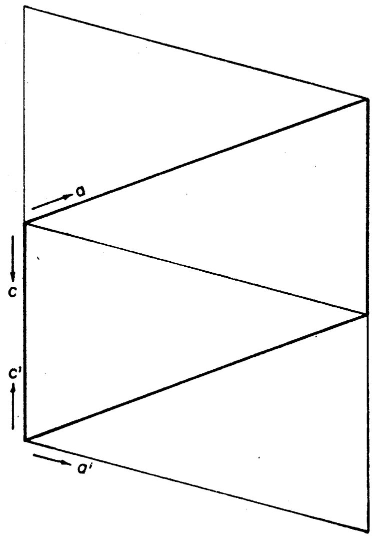

FIG. 1. $(\text{Glycine})_3 \cdot H_2SO_4$: relations between the unit cell chosen by Wood and Holden[3] and that used in this paper.

SO_4,[6] and nonisomorphous $(NH_4)_2BeF_4$,[7,8] a good number of ammonium, methylammonium or urea alums,[9–12] $(NH_4)_2Cd_2(SO_4)_3$,[13] NH_4HSO_4,[14] $Li(N_2H_5)SO_4$,[15] $NaNH_4SO_4 \cdot 2H_2O$,[16] $(\text{glycine})_2 \cdot MnCl_2 \cdot 2H_2O$,[17] $(\text{glycine})_2 \cdot HNO_3$,[18] $\text{glycine} \cdot AgNO_3$,[19] $NaH_3(SeO_3)_2$,[20] and $LiH_3(SeO_3)_2$.[21] The antiferroelectrics $NH_4PF_6 \cdot NH_4F$ [22] and NH_4I [23] are also pertinent.

In the present paper the x-ray structure determination of the room-temperature phase of $(\text{glycine})_3 \cdot H_2SO_4$ is reported, and the importance of the glycine and sulfate configuration, and H-bonding, is demonstrated.

EXPERIMENTAL

The crystals of $(\text{glycine})_3 \cdot H_2SO_4$ used in the present x-ray study were grown from aqueous solution of the components in stoichiometric molar ratio. The symmetry and optical properties of this crystal were earlier reported by Wood and Holden.[3] We have selected axial settings which simplify description of the forms observed on most of the large crystals grown from aqueous solution. From standard x-ray measurements we find $a = 9.41_7$ A, $b = 12.64_3$ A, $c = 5.73_5$ A, $\beta = 110° 23'$. There are two chemical units per cell, and the space group is uniquely established as $P2_1$ by systematic absences of x-ray reflections and the ferroelectric behavior. The a and c axes selected by us, as preferable on physical grounds, are related to those of Wood and Holden by the transformation formulae $a = a' + c'$, $b = b'$, and $c = -c'$, where the primed axes are those reported by Wood and Holden. The relations between the two cells are illustrated in Fig. 1.

Three-dimensional intensity data were obtained from equi-inclination Weissenberg photographs using the multiple-film technique (6 sheets of Kodak Medical No-Screen X-Ray Film). The crystals were rotated around the a axis ($h = 0$), around the b axis ($k = 0$ to 9), and around the c axis ($l = 0$ to 5). In all, about 1460 nonequivalent reflections were recorded using Cu $K\alpha$ radiation. The intensities of the reflections were estimated visually by comparison with a standard scale. They were corrected for the usual Lorentz and polarization factors. Due to the small linear absorption coefficient and the small radii of the cylindrical specimens (less than 0.1 mm), no absorption correction was made. Some reflections with strong intensities were affected by extinction. Corrections for the secondary extinction were made at the later stage of refinement through comparison with calculated structure factors, in a manner described below.

STRUCTURE DETERMINATION

Since the ferroelectric phase of $(\text{glycine})_3 \cdot H_2SO_4$ belongs to the space group $P2_1$ and the number of chemical units in the unit cell is two, coordinates of all the atoms in a chemical unit had to be determined. However, the structure cannot differ greatly from that of the paraelectric phase with centrosymmetric space group $P2_1/m$, which has four-fold general positions, and two-fold special positions within the mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. This is confirmed by the smallness of differences observed between intensities of reflections from the ferroelectric phase and corresponding reflections from the paraelectric phase. Therefore, in the first stage of the structure analysis, one of the three glycine molecules and the sulfur atom were placed in the mirror plane. The remaining two glycine molecules and the orientation of the sulfate ion were assumed to be in positions satisfying mirror symmetry.

The structure determination was initiated by determining the position of the sulfur atom, by referring to the position of the selenium atom in isomorphous $(\text{glycine})_3 \cdot H_2SeO_4$. Projections of the Patterson function along the b and c axes for the selenate were computed on *X-RAC*, and the coordinates of the selenium atom were readily established as (0.00, 0.25, 0.24).

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[23] R. Pepinsky (unpublished).

These values were used to determine the signs of F_{h0l} coefficients by comparing those of the sulfate and of the selenate crystal, using the following relation:

$$(F_{h0l})_{\text{sulfate}} = (F_{h0l})_{\text{sulfur}} + (F_{h0l})_{\text{rest}},$$

and

$$(F_{h0l})_{\text{selenate}} = (F_{h0l})_{\text{selenium}} + (F_{h0l})_{\text{rest}},$$

where $(F_{h0l})_{\text{rest}}$ refers to the contributions of the lighter atoms, which were assumed to be the same for the two crystals. Although the fact, that the sulfur or selenium atom does not contribute to the $(h0l)$ reflections with odd l indices, made it easy to put the two sets of data on the same scale, the signs of the reflections with l odd could not be determined at all by this isomorphous replacement method. Therefore a number of trial models were tested, based on the structure deduced from the F_{h0l} reflections with l even, plus *one* F_{h0l} reflection with l odd; the latter was $F_{\bar{2}01}$, whose sign could arbitrarily be assigned as positive. After several calculations using *X-RAC* and *S-FAC*, the structure appeared to converge properly.

Since the projection along the b axis was fairly well determined, attention was focussed on determination of the y coordinates. Assuming mirror symmetry in the crystal, at first only the y coordinates of the two glycine molecules which do not lie in the mirror plane needed to be determined. These glycine molecules were placed in such a manner that all the interatomic distances became reasonable. After several iterated structure-factor and electron-density calculations on *S-FAC* and *X-RAC*, a reasonable agreement was obtained between F_{obs} and F_{calc}.

At this stage, the deviation of the structure from the centrosymmetric space group became apparent, by an unreasonable distortion of the sulfate ion and also by elongation of the electron density of some of the atoms of the glycine molecule. Accordingly, the provisional mirror symmetry was removed and the noncentrosymmetric space group $P2_1$ was adopted for further analysis.

TABLE I. (Glycine)$_3 \cdot H_2SO_4$: atomic coordinates, their standard deviations σ (in fractions of cell edges), and temperature factors B (in A^2).

Atoms	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
(Sulfate ion)							
S	0.9995	0.0002	0.2500	0.0001	0.2250	0.0002	0.33
O_1	0.8583	0.0005	0.2447	0.0006	0.0051	0.0009	1.56
O_2	0.9669	0.0006	0.2437	0.0006	0.4572	0.0009	1.83
O_3	1.0920	0.0005	0.1565	0.0006	0.2234	0.0009	1.48
O_4	1.0769	0.0006	0.3469	0.0006	0.1941	0.0009	2.27
(Glycine I)							
O	0.6064	0.0007	0.2393	0.0005	1.0746	0.0010	2.66
O′	0.4935	0.0009	0.2718	0.0008	0.6668	0.0011	3.39
C	0.4905	0.0010	0.2472	0.0010	0.8727	0.0017	2.75
C^N	0.3348	0.0010	0.2361	0.0010	0.9049	0.0017	2.78
N	0.3595	0.0013	0.2110	0.0012	1.1639	0.0018	3.86
(Glycine II)							
O	0.2218	0.0006	0.4975	0.0006	0.7646	0.0009	1.79
O′	0.4596	0.0008	0.5397	0.0008	0.7988	0.0011	3.23
C	0.3153	0.0010	0.5331	0.0010	0.6797	0.0016	2.82
C^N	0.2675	0.0012	0.5734	0.0011	0.4070	0.0017	3.29
N	0.0939	0.0008	0.5800	0.0008	0.3063	0.0012	2.39
Glycine III)							
O	0.7824	0.0007	0.4931	0.0007	0.2229	0.0011	2.76
O′	0.5454	0.0007	0.4825	0.0007	0.2317	0.0011	2.57
C	0.6937	0.0007	0.4749	0.0007	0.3281	0.0011	1.32
C^N	0.7440	0.0007	0.4320	0.0007	0.5906	0.0011	1.27
N	0.9068	0.0006	0.4331	0.0006	0.7059	0.0009	1.06

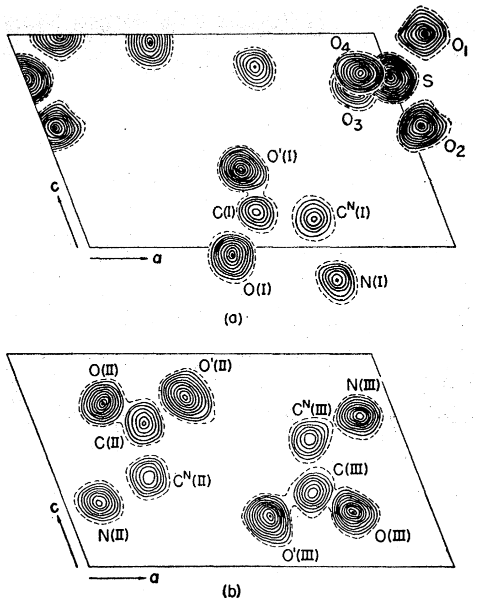

FIG. 2. (Glycine)$_3 \cdot H_2SO_4$: composite diagrams of the three-dimensional electron-density function viewed along the b axis: (a) atoms near the plane $y=\frac{3}{4}$; (b) atoms near the plane $y=\frac{1}{2}$. Contours are drawn at intervals of 1.5 e/A^3 beginning at 2.0 e/A^3 which are shown by broken lines. The sulfur atom has contours at intervals of 3.0 e/A^3.

REFINEMENT OF THE STRUCTURE

All the atomic coordinates except those for hydrogen atoms, as obtained by the procedures described in the previous section, were subjected to least-squares refinement using the automatic refinement program *NYXR3* of Vand and Pepinsky[24] on the IBM-704 data-processing machine. In the course of these refinements, it was found that several reflections with strong intensities were affected considerably by the extinction effect, and these F_{obs}'s were corrected for secondary extinction using the usual formula

$$F_{\text{obs}}^{\text{corrected}} = F_{\text{obs}} \exp(gF^2_{\text{calc}}Lpf)$$

(all symbols have usual meanings), with $g = 1.05 \times 10^{-5}$. After five cycles the disagreement factor,

$$R = \Sigma \| F_{\text{obs}} | - | F_{\text{calc}} \| / \Sigma | F_{\text{obs}} |,$$

dropped to 0.167 for the three-dimensional reflection data including the nonobserved reflections.

The final set of atomic coordinates and isotropic temperature factor is given in Table I. The standard deviations of the atomic coordinates have been estimated using the formula by Cruickshank[25] and are also listed in Table I. Composite diagrams of the three-dimensional electron-density function are shown in Figs. 2(a) and 2(b). The electron-density projection

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[24] V. Vand and R. Pepinsky, Z. Krist. **111**, 46 (1958).

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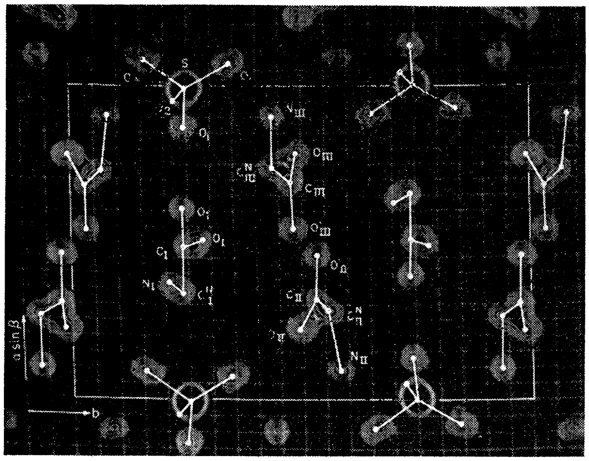

FIG. 3. (Glycine)$_3$·H_2SO_4: projection of electron-density function along the c axis. Contours are drawn on an arbitrary scale with equal intervals. Atoms in one asymmetric unit are marked.

along the c axis, using the final set of the phases of structure factors, is shown in Fig. 3. Comparison between the observed and calculated structure factors is given in a supplementary table.[26]

Interatomic distances and some of the important angles have been calculated using the coordinates in Table I. They will be dealt with later in connection with the discussion of the structure.

DISCUSSION OF THE RESULTS

(a) The Sulfate Ion

The shape and size of the sulfate ion in (glycine)$_3$·H_2SO_4 are shown in Figs. 4(a) and 4(b). The observed S–O separations, which range from 1.46_7 to 1.48_1 A- are comparable to those found in the structure of mono, methylammonium aluminium alum,[27] where the sulfate ion possesses three-fold symmetry and the S–O separation on the symmetry axis is found to be 1.49_4 A and the remaining three separations are 1.47_3 A. It might be worthwhile to note here that in the crystal structures of inorganic sulfates such as $KHSO_4$[28] and $MgSO_4$[29] the S–O distances are always longer than 1.50 A, and the value of 1.51 A given by Pauling[30] still seems to be valid. Whether or not this difference in the S–O distances is due to the hydrogen bonds formed by the organic parts of the crystal is still not clear, since examples of accurate structure analyses of organic-ion sulfates are rare.

The deviation of the sulfate ion from the tetrahedral symmetry was also observed by the measurements of the Raman lines of the crystal (Krishnan and Balasubramanian[31]; Taurel, Delain, and Guerin[32]). Instead of four frequency shifts expected for the perfect tetrahedral group, nine shifts which can be assigned to the internal oscillation of the sulfate ion were observed by Krishnan and Balasubramanian.[31] From this, it is apparent that the degeneracies of the frequencies due to the tetrahedral symmetry have been removed.

In contrast to the structure of monomethylammonium aluminium alum, where the O–S–O angles are all tetrahedral within the experimental error, the O–S–O angles in the present crystal range from 105° to 115°. This is not unreasonable, since hydrogen bonds of apparently unequal strength exist between the sulfate oxygens and other atoms, and these might force the distortion of the sulfate ion.

(b) The Glycine Ions

Bond distances and angles in the three glycine ions are shown in Fig. 5. For comparison, the corresponding data for the glycine zwitter-ion in the crystal of α-glycine[33] are also shown in that figure. The configurations of these glycine ions are studied by evaluating the equations of planes including the carboxyl group and the carbon atom C^N by the method of least squares. These equations are

$$X-44.660_7Y-9.844_6Z+170.260_9=0 \text{ for (glycine)}_{\text{I}},$$

$$X-7.151_4Y-2.930Z+53.763_0=0 \text{ for (glycine)}_{\text{II}},$$

and

$$X+5.111_3Y-0.391_4Z-36.461_7=0 \text{ for (glycine)}_{\text{III}}.$$

The three variables X, Y, and Z are represented as $X=ax\sin\beta$, $Y=by$, and $Z=cz-ax\cos\beta$, where x, y, and z are measured in fractions of cell edges. The displacements of the atoms from these planes are shown

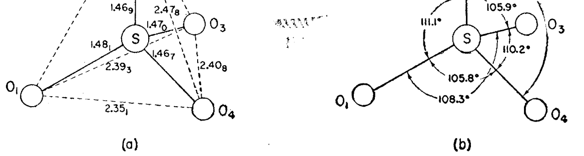

FIG. 4. (Glycine)$_3$·H_2SO_4: the size and the shape of the sulfate ion: (a) bond distances; (b) bond angles.

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[26] This supplementary table has been deposited as Document No. 5997 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $5.00 for photoprints, or $2.25 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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[32] Taurel, Delain, and Guerin, Compt. rend. **246**, 3042 (1958).

[33] R. E. Marsh, Acta Cryst. **11**, 654 (1958).

in Table II, where the negative values mean that the atom and the origin lie on the same side of the plane.

The displacements of the nitrogen atoms from the planes are of importance in this crystal structure. In the crystal of α-glycine, where the glycine definitely possesses the zwitter-ion structure, the nitrogen atom is displaced from the plane containing the remaining four atoms by 0.436 A.[33] Moreover, in the crystal structure of (glycine)$_2$·HCl,[34] where the chemical formula is clearly $(NH_3^+CH_2COO^-)\cdot(NH_3^+CH_2COOH)\cdot Cl^-$, it was found that two types of glycine ions are present in the crystal; one type takes the almost complete planar configuration as (glycine)$_{I}$ or (glycine)$_{III}$, and in the glycine of the other type the nitrogen atom is displaced from the molecular plane by 0.33 A. Similar characteristics are also found in the crystal of (glycine)$_2$·HBr.[35] From the above considerations, it can safely be assumed the correct chemical formula for (glycine)$_3$·H$_2$SO$_4$ is $(NH_3^+CH_2COOH)_2\cdot(NH_3^+CH_2COO^-)\cdot SO_4^{--}$ and the monoprotonated glycines I and III take the first configuration, while the remaining glycine II takes the zwitter-ion configuration. As is to be expected, the sulfate ion has lost both of its protons. Thus glycines I and III are best designated as glycinium ions, while the zwitter-ion glycine II is simply designated as glycine. It is for this reason that we designate the compound as glycine diglycinium sulfate.

All the bond distances and angles in the glycine ions are more or less normal, except for the C_{II}^N–N_{II} distance of 1.53$_5$ A, which appears to be a little longer than the reported value of 1.52$_1$ A in the glycinium ion in (glycine)$_2$·HCl.[34] For glycines I and III these bond distances are similar to those for the glycine zwitter-ion in α-glycine, except for the slight inequality of the C–O bonds in the carboxyl groups. No effort is made at this time to explain the variations in bond length; the hydrogen-bond system in this crystal is complex, and will be discussed fully after completion of a neutron analysis presently in progress.

(c) The Hydrogen-Bond System

The projection of the structure along the *c* axis is shown in Fig. 6. Proposed hydrogen bonds are illustrated by chain lines; dashed lines indicate other short approaches. Distances and the Donohue angles[36] for all the important short approaches were calculated and are listed in Table III. Since more than one asymmetric unit is involved in the complicated hydrogen-bond

TABLE II. Displacements of the atoms from the planes of the glycine molecules (in A).

Glycine	I (glycinium)	II (zwitter-ion)	III (glycinium)
N	0.00$_4$	−0.26$_9$	−0.00$_1$
C^N	0.00$_9$	0.00$_2$	−0.04$_4$
C	0.03$_5$	−0.00$_6$	0.00$_5$
O	−0.01$_3$	0.00$_3$	0.04$_9$
O′	−0.01$_2$	0.00$_2$	−0.01$_8$

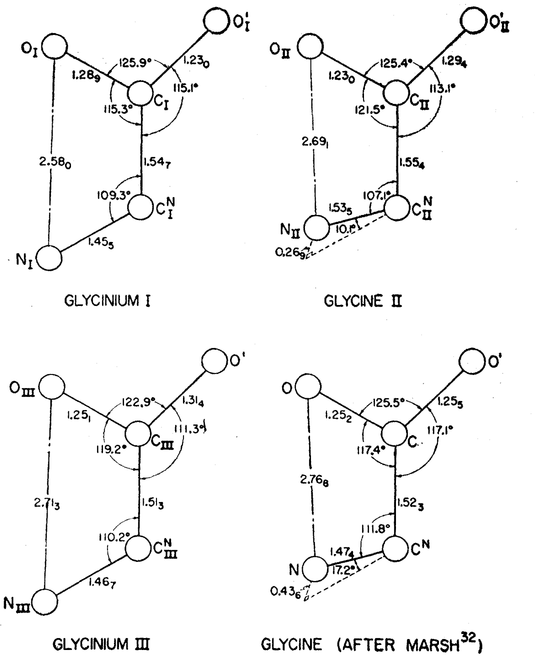

FIG. 5. (Glycine)$_3$·H$_2$SO$_4$: bond distances and angles in the glycine ions. The values obtained for the glycine zwitter-ion in the crystal of α-glycine [Marsh[33] (incorrectly cited in the figure as Marsh[32])] are also shown for comparison.

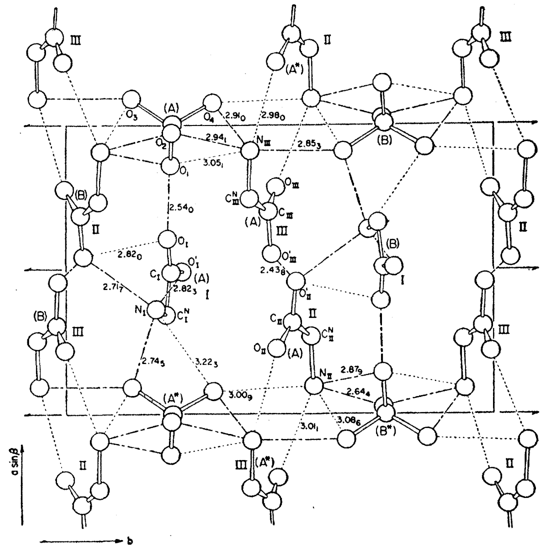

FIG. 6. (Glycine)$_3$·H$_2$SO$_4$: projection of the structure along the *c* axis. Proposed hydrogen bonds are shown by chain lines, and other short approaches are indicated by dashed lines. Distances are in A. The symbols adopted in this figure are explained in the text.

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[35] Buerger, Barney, and Hahn, Z. Krist. **108**, 130 (1956).

[36] J. Donohue, J. Phys. Chem. **56**, 502 (1952).

networks, the following notations were employed. The atoms with the coordinates in Table I are designated by the symbol A. The equivalent points derived from the above coordinates by the two-fold screw axis are denoted by the symbol B; however, for the sake of simplicity the atoms near the plane $y=\frac{1}{4}$ are moved along the positive b direction and those near the plane $y=\frac{1}{2}$ are moved along the negative direction. This will easily be seen from Fig. 6. All the atoms which are one unit cell below along the c direction are designated by single primes; those one unit cell above along c are marked by double primes. The atoms with an asterisk are in the next cell in the direction of a. The glycinium ion $\mathrm{I}(A)$ which lies near the plane $y=\frac{1}{4}$ makes one $O-H\cdot\cdot O$ and three $N-H\cdot\cdot O$ hydrogen bonds. The oxygen atom of the carboxyl group which apparently possesses a hydrogen atom makes a fairly short hydrogen bond of 2.54_0 A to $O_1(A)$ of the sulfate ion. Three hydrogen bonds are made by the nitrogen atom $N_{\mathrm{I}}(A)$: 2.74_5 A to $O_3(A^*)$, 2.82_3 A to $O_{\mathrm{I}}'(A'')$ and 2.71_7 A to $O_{\mathrm{II}}'(B'')$. The nitrogen atom $N_{\mathrm{I}}(A)$ thus makes the three hydrogen bonds which are pyramidally arranged; the angles between these bonds vary from 92° to 97°. A short approach of 2.82_0 A is observed between $O_{\mathrm{I}}(A)$ and $O_{\mathrm{II}}'(B)$; however, in view of the Donohue angles and also of the number of available hydrogen atoms, this approach cannot be considered as hydrogen-bonded.

TABLE III. (Glycine)$_3\cdot H_2SO_4$: short intermolecular distances (in A) and related Donohue angles (in degrees).

Distances		Angles	
$O_{\mathrm{I}}(A)\text{–}O_{\mathrm{II}}'(B'')$	2.82_0	$C_{\mathrm{I}}(A)\text{–}O_{\mathrm{I}}(A)\text{–}O_{\mathrm{II}}'(B'')$	93.4
		$O_{\mathrm{I}}(A)\text{–}O_{\mathrm{II}}'(B'')\text{–}C_{\mathrm{II}}(B'')$	81.9
$O_{\mathrm{I}}(A)\text{–}O_1(A'')$	2.54_0[a]	$C_{\mathrm{I}}(A)\text{–}O_{\mathrm{I}}(A)\text{–}O_1(A'')$	113.7
		$O_{\mathrm{I}}(A)\text{–}O_1(A'')\text{–}S(A'')$	118.6
$N_{\mathrm{I}}(A)\text{–}O_3(A^{*\prime\prime})$	2.74_5[a]	$C_{\mathrm{I}}^{N}(A)\text{–}N_{\mathrm{I}}(A)\text{–}O_3(A^{*\prime\prime})$	110.5
		$N_{\mathrm{I}}(A)\text{–}O_3(A^{*\prime\prime})\text{–}S(A^{*\prime\prime})$	111.7
$N_{\mathrm{I}}(A)\text{–}O_{\mathrm{II}}'(B'')$	2.71_7[a]	$C_{\mathrm{I}}^{N}(A)\text{–}N_{\mathrm{I}}(A)\text{–}O_{\mathrm{II}}'(B'')$	97.3
		$N_{\mathrm{I}}(A)\text{–}O_{\mathrm{II}}'(B'')\text{–}C_{\mathrm{II}}(B'')$	127.4
$N_{\mathrm{I}}(A)\text{–}O_{\mathrm{I}}'(A'')$	2.82_3[a]	$C_{\mathrm{I}}^{N}(A)\text{–}N_{\mathrm{I}}(A)\text{–}O_{\mathrm{I}}'(A'')$	147.1
		$N_{\mathrm{I}}(A)\text{–}O_{\mathrm{I}}'(A'')\text{–}C_{\mathrm{I}}(A'')$	139.5
$O_{\mathrm{II}}'(A)\text{–}O_{\mathrm{III}}'(A'')$	2.43_8[a]	$C_{\mathrm{II}}(A)\text{–}O_{\mathrm{II}}'(A)\text{–}O_{\mathrm{III}}'(A'')$	115.7
		$O_{\mathrm{II}}'(A)\text{–}O_{\mathrm{III}}'(A'')\text{–}C_{\mathrm{III}}(A'')$	112.1
$N_{\mathrm{II}}(A)\text{–}O_2(B^*)$	2.64_4[a]	$C_{\mathrm{II}}^{N}(A)\text{–}N_{\mathrm{II}}(A)\text{–}O_2(B^*)$	104.0
		$N_{\mathrm{II}}(A)\text{–}O_2(B^*)\text{–}S(B^*)$	131.2
$N_{\mathrm{II}}(A)\text{–}O_4(A^*)$	3.00_9[a]	$C_{\mathrm{II}}^{N}(A)\text{–}N_{\mathrm{II}}(A)\text{–}O_4(A^*)$	94.4
		$N_{\mathrm{II}}(A)\text{–}O_4(A^*)\text{–}S(A^*)$	141.6
$N_{\mathrm{II}}(A)\text{–}O_{\mathrm{III}}(A^*)$	3.01_1	$C_{\mathrm{II}}^{N}(A)\text{–}N_{\mathrm{II}}(A)\text{–}O_{\mathrm{III}}(A^*)$	149.9
		$N_{\mathrm{II}}(A)\text{–}O_{\mathrm{III}}(A^*)\text{–}C_{\mathrm{III}}(A^*)$	139.0
$N_{\mathrm{II}}(A)\text{–}O_1(B^{*\prime})$	2.87_9[a]	$C_{\mathrm{II}}^{N}(A)\text{–}N_{\mathrm{II}}(A)\text{–}O_1(B^{*\prime})$	100.8
		$N_{\mathrm{II}}(A)\text{–}O_1(B^{*\prime})\text{–}S(B^{*\prime})$	105.8
$N_{\mathrm{II}}(A)\text{–}O_3(B^{*\prime})$	3.08_6	$C_{\mathrm{II}}^{N}(A)\text{–}N_{\mathrm{II}}(A)\text{–}O_3(B^{*\prime})$	123.6
		$N_{\mathrm{II}}(A)\text{–}O_3(B^{*\prime})\text{–}S(B^{*\prime})$	97.1
$N_{\mathrm{III}}(A)\text{–}O_2(A)$	2.94_1[a]	$C_{\mathrm{III}}^{N}(A)\text{–}N_{\mathrm{III}}(A)\text{–}O_2(A)$	96.5
		$N_{\mathrm{III}}(A)\text{–}O_2(A)\text{–}S(A)$	122.1
$N_{\mathrm{III}}(A)\text{–}O_3(B)$	2.85_3[a]	$C_{\mathrm{III}}^{N}(A)\text{–}N_{\mathrm{III}}(A)\text{–}O_3(B)$	90.7
		$N_{\mathrm{III}}(A)\text{–}O_3(B)\text{–}S(B)$	140.2
$N_{\mathrm{III}}(A)\text{–}O_{\mathrm{II}}(A^*)$	2.98_0	$C_{\mathrm{III}}^{N}(A)\text{–}N_{\mathrm{III}}(A)\text{–}O_{\mathrm{II}}(A^*)$	152.7
		$N_{\mathrm{III}}(A)\text{–}O_{\mathrm{II}}(A^*)\text{–}C_{\mathrm{II}}(A^*)$	151.3
$N_{\mathrm{III}}(A)\text{–}O_1(A'')$	3.06_1	$C_{\mathrm{III}}^{N}(A)\text{–}N_{\mathrm{III}}(A)\text{–}O_1(A'')$	84.3
		$N_{\mathrm{III}}(A)\text{–}O_1(A'')\text{–}S(A'')$	100.2
$N_{\mathrm{III}}(A)\text{–}O_4(A'')$	2.91_0[a]	$C_{\mathrm{III}}^{N}(A)\text{–}N_{\mathrm{III}}(A)\text{–}O_4(A'')$	124.1
		$N_{\mathrm{III}}(A)\text{–}O_4(A'')\text{–}S(A'')$	107.4

[a] Proposed hydrogen bonds (see text).

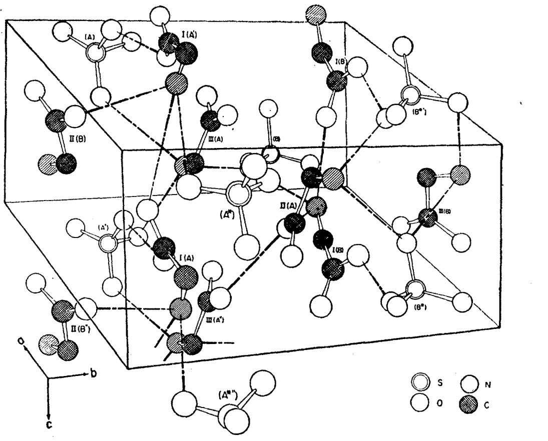

FIG. 7. (Glycine)$_3\cdot H_2SO_4$: clinographic projection of the structure, showing the hydrogen-bond system. N atoms are indicated by diagonally shaded circles.

The two glycine molecules near the plane $y=\frac{1}{2}$ exhibit a strong $O-H\cdot\cdot O$ hydrogen bond, with a short separation of 2.43_8 A between $O_{\mathrm{III}}'(A)$ and $O_{\mathrm{II}}'(A'')$. As will be discussed later, this strong hydrogen bond must play a most important role in the ferroelectricity of this crystal. The physical importance of similar short $O-H\cdot\cdot O$ hydrogen bonds is well known in the crystals of potassium and ammonium dihydrogen phosphates.[37–43]

The hydrogen-bond systems around the nitrogen atoms of these two glycine ions are rather involved. There are five short N–O distances around each nitrogen atom: around N_{II} one finds $N_{\mathrm{II}}(A)\text{–}O_2(B^*)$, $N_{\mathrm{II}}(A)\text{–}O_1(B^{*\prime})$, $N_{\mathrm{II}}(A)\text{–}O_3(B^{*\prime})$, $N_{\mathrm{II}}(A)\text{–}O_4(A^*)$, and$N_{\mathrm{II}}(A)\text{–}O_{\mathrm{III}}(A^*)$, with distances 2.64_4 A, 2.87_9 A, 3.08_6 A, 3.00_9 A, and 3.01_1, A, respectively. Similar arrangements are also found around the nitrogen atom on the glycinium III, although the distances vary slightly as shown in Fig. 6. Out of the five short distances around the $N_{\mathrm{II}}(A)$ atom, the first two are considered to be hydrogen-bonded in view of the distances as well as the Donohue angles; however, it is difficult to decide by

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[37] B. C. Frazer and R. Pepinsky, Acta Cryst. **6**, 273 (1953).

[38] Peterson, Levy, and Simonsen, J. Chem. Phys. **21**, 2084 (1953).

[39] G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A220**, 397 (1953).

[40] G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A230**, 359 (1955).

[41] Levy, Peterson, and Simonsen, Phys. Rev. **93**, 1120 (1954).

[42] R. O. Keeling and R. Pepinsky, Z. Krist. **106**, 236 (1955).

[43] Tenzer, Frazer, and Pepinsky, Acta Cryst. **11**, 505 (1958).

x-rays which one of the remaining short approaches is hydrogen-bonded. A neutron diffraction study at Brookhaven National Laboratory has confirmed the presence of hydrogen bonds between $N_{II}(A)$ and $O_2(B^*)$, $N_{II}(A)$ and $O_1(B^{*\prime})$ and $N_{II}(A)$–$O_4(A^*)$. These results will separately be reported.

Around the nitrogen atom $N_{III}(A)$, the three approaches $N_{III}(A)$–$O_2(A)$, $N_{III}(A)$–$O_4(A'')$, and $N_{III}(A)$–$O_3(B)$, with distances 2.94_1 A, 2.91_0 A, and 2.85_3 A, respectively, are considered as hydrogen-bonded. All the observed $N-H\cdot\cdot O$ hydrogen bonds as well as the van der Waals contacts in this crystal show normal distances. In Fig. 7 a clinographic projection of the structure is presented. This also shows the hydrogen-bond arrangement.

(d) Possible Interpretation of the Ferroelectric Behavior

(Glycine)$_3$·H$_2$SO$_4$ is ferroelectric at room temperature,[1] and the Curie point is 47°C. As is evident from the symmetry, the b axis is polar. In the ferroelectric crystal, it is necessary that certain dipoles should be capable of easy reversal upon application of an electric field. The structure investigation shows that the main reversible dipole is associated with the completely planar glycinium ion I, whose molecular plane makes an angle of 12.5° with the plane $y=\frac{1}{4}$. It can be seen from the above structure, glycinium I is nearly symmetrically surrounded by oxygen atoms of the sulfate ions and from the other glycine molecules, in such a way that the plane of glycinium ion I can take another orientation which is related to the original orientation by the provisional mirror planes at $y=\frac{1}{4}$ and $\frac{3}{4}$. These planes become the mirror planes, statistically only, above the Curie point, by the statistical arrangement of the glycinium I ions.

The short $O-H\cdot\cdot O$ bond between $O_{III}'(A)$ and $O_{II}'(A'')$ is of fundamental importance in the switching mechanism. The separation of 2.43_8 A suggests that the hydrogen must be shared almost equally between these two ions. The configuration shown in Fig. 6 suggests that the hydrogen is actually more closely allied with the planar glycinium ion III, in the polarization state shown there. When it is so associated, glycine II is the zwitter-ion ^+H_3N–CH_2COO^-, and the $-NH_3^+$ group is out of the plane of the two C and two O atoms. A reversal of the H association from ion III to ion II carries with it a reversal of the former glycinium-glycine roles of these two ions; and this reversal is accompanied by changes in the $-NH_3^+$ positions in the two ions.

In the above described mechanism, the actual change in hydrogen position is *assumed*, on the basis of the short $O_{III}'(A)$–$O_{II}'(A'')$ separation and the known configurations of glycinium and zwitter-ion glycines in other structures, and the clearly-revealed positions of the $-NH_3^+$ groups with respect to the planes of the remaining C and O atoms in these ions in the present structure. It is comforting to be able to report that the neutron analysis at Brookhaven Laboratory, referred to above in connection with the problem of H-bonding around N_{II}, entirely supports the conclusion based on this x-ray study. *It shows the hydrogen between* $O_{III}'(A)$ *and* $O_{II}'(A'')$ *in a position closer to* $O_{III}'(A)$ *than to* $O_{II}'(A'')$. This asymmetry in the hydrogen position is remarkable, in the case of such a short separation between the oxygens.

The dipole reversal mechanism here is extremely interesting. It illustrates the close coupling between changes in any part of the structure with changes in any other part. The deduced "flipping" of the tightly-bonding hydrogen between O_{II}' and O_{III}', which is coupled with the change from a noncoplanar glycine zwitter-ion to a planar mono-protonated glycinium ion, with associated rotation of sulfate ions, helps to account for the large spontaneous polarization. This "flipping" is confirmed by the neutron study. These changes cause a transfer of H-bonding between N_I and one of the sulfate oxygens to an H-bond between the same N_I and the other SO$_4$ oxygen. This change avoids the necessity for a "bifurcated" H-bond between N_I and the two sulfate oxygens. In the paraelectric structure a "bifurcated" bond is also unnecessary, due to the disorder of the structure.

The switching of the dipoles is illustrated schematically in Fig. 8.

The absolute configurations of this crystal and its isomorphs under an electric field are being studied using the technique of anomalous x-ray dispersion,[44,45] in order to establish the relation between the direction

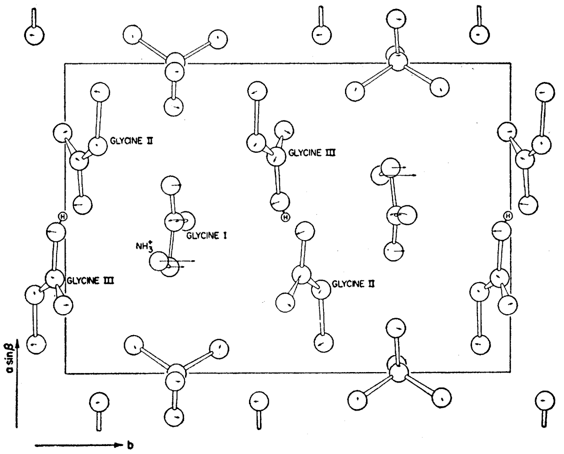

FIG. 8. (Glycine)$_3$·H$_2$SO$_4$: schematic drawings of the structure illustrating the switching of the direction of ferroelectric dipoles. The arrows show the positions to which the various atoms have moved after reversal of the polar axis.

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[44] R. Pepinsky and Y. Okaya, Proc. Natl. Acad. Sci. (U.S.) **42**, 246 (1956).

[45] R. Pepinsky, Record Chem. Progr. Kresge-Hooker Sci. Lib. **17**, 145 (1956).

of the applied field and that of the ferroelectric dipole. It has already been ascertained, by these measurements, that the polarization state shown in Fig. 8, disregarding the arrows from the atom centers, corresponds to a field and spontaneous polarization in the *negative b* direction. When the atoms move as indicated by the arrows, the polarization direction is along the *positive b* axis.

Previous dielectric and thermal studies[4] suggested that the transition is of order-disorder type. Preliminary x-ray examination of the paraelectric phase confirms this. The temperature dependence of the spontaneous polarization, and the second-order character of the transition, suggest that at the temperature of our x-ray observations, about 20°C, a certain degree of disorder must persist in the structure. This disorder has not as yet been taken into account in the structure analysis. Detailed x-ray and neutron studies of the structures on either side of the Curie point are in progress. A very important approach to this order-disorder problem is *via* study of the x-ray diffuse scattering. Such a study, both theoretical and experimental, is in progress. A theoretical treatment of various physical properties, based upon the structure reported here, is presented elsewhere.[46]

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[46] Mitsui, Shibuya, and Pepinsky (to be published).

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Surface States in Metals*

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This paper deals with measurements of conductivity modulation in metals by an electric field. The measurements have been performed using a new technique, which permits reaching an accuracy sensibly higher than that obtained in experiments already published.

Measurements on Au, Sb, and Bi films have been carried out at different temperatures between about −20 and +80°C. The existence of localized and conducting "surface states" at the metal/dielectric interface seems to be experimentally confirmed.

(1) INTRODUCTION

EXPERIMENTS on the modulation of conductivity by electrical charges induced at the surface of a flat metal specimen by a transverse electric field, strictly analogous—in principle—to those performed on semiconductors,[1] were reported in a paper already published by the present authors.[2]

The specimens used were in form of thin films; this was necessary in order to obtain measurable effects in spite of the enormous density of the charge carriers in a metal. The specimens were connected across an arm of a high-sensitivity Wheatstone bridge. At the same time they were used as one of two metal plates of a flat mica condenser, charged by a high-voltage power supply that produced a transverse electric field inducing a large surface charge on the specimen. The specimens (in the form of thin films of the order of magnitude 100 or 1000 A thick, according to the metal considered) were evaporated on a convenient mica support. Unusual results were found for Au, Bi, and Sb, that is, for metals of widely different electronic structure.

In the present paper, we report a new series of measurements which have been performed using a different detection technique which has inherent advantages and higher accuracy. Furthermore, a point of utmost importance has been investigated, namely, the dependence of the effect on temperature. It has been possible to explore the range between −20° and +80°C, where interesting effects have been found. For this purpose, an ultrathermostat has been used, with an over-all stability of better than 10^{-2}°C.

The results obtained seem to lead to the hypothesis that "surface" electronic states of both localized and conducting type are present at the metal (specimen)/dielectric (mica support) interface.

(2) EXPERIMENTAL TECHNIQUE

(a) Specimens

In the preparation of the specimens, two points have been cared for in a more refined manner than in our previous experiments,[2] to which the reader is referred for all the technical details which are not given here. First, the evaporations have been carried out in a better

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[1] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 29 ff.

[2] Bonfiglioli, Coen, and Malvano, Phys. Rev. **101**, 1281 (1956).

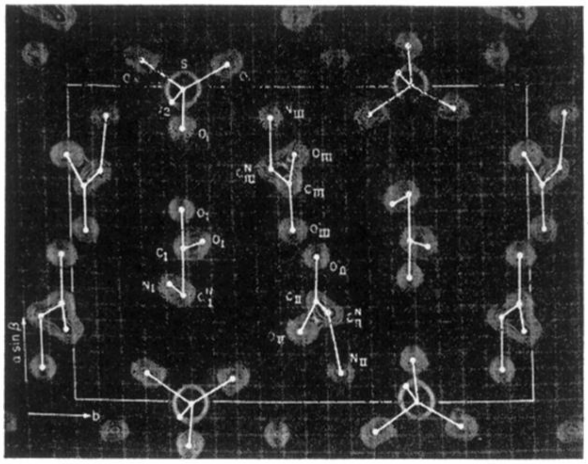

FIG. 3. (Glycine)$_3 \cdot H_2SO_4$: projection of electron-density function along the *c* axis. Contours are drawn on an arbitrary scale with equal intervals. Atoms in one asymmetric unit are marked.