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Ferroelectric Behavior of Thiourea

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The dielectric constant, and the ferroelectric, pyroelectric, and piezoelectric properties of thiourea crystals have been measured in the temperature range 90°K to 300°K. At least three dielectric anomalies are found at 169°K, 177°K, and 202°K, the lowest of these corresponding to a pronounced discontinuity. The crystals are ferroelectric in two regions, below 169°K and between 176°K and 180°K. Substitution of deuterium for hydrogen causes the anomalies to move upwards in temperature by 16°, 16°, and 11°, respectively. The crystal structure has been determined in detail at 120°K in the lower ferroelectric region. The transition from the antiferroelectric room temperature structure to the ferroelectric state is accomplished by small rotations of the molecules such that two of the molecules in the crystal unit cell have tilts to the ferroelectric b axis appreciably different from the other two, and the resultant of the molecular dipoles along [010] is no longer zero. The ferroelectric reversal is thus easily accomplished by interchanging the tilts of the two pairs of molecules.

I. INTRODUCTION

DERROELECTRICITY in thiourea, $SC(NH_2)_2$, was first reported by A. L. Solomon in 1957.¹ In the work now described, we have found that this material is unique among known ferroelectrics in that it forms a molecular crystal, the ferroelectric behavior being associated with relative displacements of entire molecules rather than in motion of ions within the crystal. The room temperature structure could be regarded as an antiferroelectric configuration, and over a temperature range between 169°K and 198°K there are four anomalies in the dielectric constant. There are two temperature ranges over which thiourea exhibits ferroelectricity, one of which lies between two nonferroelectric states. The crystallographic transition corresponding to the highest temperature anomaly represents one between two antiferroelectric structures.

In this paper, the various aspects of the dielectric and ferroelectric behavior of this material are described, and the structural origin of the ferroelectric state in the temperature range below 169°K is demonstrated. Further, the influence on the electrical properties of the substitution of deuterium for hydrogen is discussed.

II. ELECTRICAL PROPERTIES

A. Crystal Preparation

Single crystals of thiourea were grown from a saturated methanol solution by slow evaporation at 30°C. Methanol was employed as the solvent rather than water, in spite of the high solubility of thiourea in the latter medium, because aqueous grown thiourea crystals are invariably cloudy and contain much occluded solvent. The evaporation rate was adjusted so that crystals of centimeter dimensions were formed over a period of several weeks.

The crystals form as orthorhombic six-sided prisms oriented as shown in Fig. 1. They exhibit distinct

¹ A. L. Solomon, Phys. Rev. 104, 1191 (1956).

cleavage in the plane perpendicular to [010] which is the ferroelectric direction.

Specimens for electrical measurement were prepared by cleaving suitable samples, about 0.2 mm thick, and applying either painted-on aquadag electrodes or evaporated gold or silver. There appears to be little difference in the performance of crystals having electrodes of different materials. The metallic electrodes, however, do result frequently in unreliable contact in the ferroelectric ranges, evidently because of piezodistortion of the crystals which causes detachment of portions of the electrodes. In addition, considerable care must be taken to avoid overheating the crystal surface during evaporation, and the electroded samples must be protected from prolonged exposure to atmospheric humidity. Thiourea is decomposed by moderate heating, and in the presence of moisture reacts with silver and gold to form the respective sulfides.

B. Dielectric Measurements

The dielectric constant was measured along the various crystallographic axes at 1000 cycles by means of a conventional capacitance bridge. Through the use of a tuned null detector with 10^{-7} volt sensitivity, it was possible to operate the bridge at only a few millivolts total voltage and hence to avoid domain wall motion over substantially the entire ferroelectric range. The maximum permissible voltage was that voltage below which the dielectric losses are voltage independent. The result is a true "low field" dielectric measurement over the entire temperature range except in the immediate vicinity of the ferroelectric transitions where the coercive field approaches zero.

The sample was mounted in dry air in a thermostat, the temperature of which was controlled by a selfbalancing resistance thermometer bridge. This device permitted maintenance of the sample temperature to within $\pm 0.07^{\circ}$ C at any point between that of liquid



nitrogen and room temperature. The sample was surrounded by suitable radiation shields in order to minimize thermal gradients. As a consequence, it was reasonably certain that the sample was of uniform temperature and in equilibrium with the thermometers at each measured point.

Additional dielectric measurements were made by means of a continuous plotting technique which, although it was of considerably less absolute precision than the point-by-point plot, permitted the observation of more detail in the $\epsilon'(T)$ relationship.

The dependence on temperature of the dielectric constant along the [010] axis is shown in Fig. 2. It will be noted that there are three prominent maxima in the dielectric constant occurring at 202°K, 177°K, and 169°K, respectively, the last of which corresponds to a pronounced discontinuity. In addition, an inflection in the curve appears at 170.5°K (see insert in Fig. 2) which probably corresponds to a fourth dielectric anomaly. The peak at 177°K is very narrow, having a width at half maximum of about 0.9°.

For the purpose of further discussion, the various temperature ranges will be referred to as indicated in Fig. 2: Region I, below 169°K; Region II, between 169°K and 176°K; Region III, from 176°K to about 180°K; Region IV, 180°K to 202°K; and Region V, above 202°K.

An examination of the relationship between the reciprocal dielectric constant and the temperature discloses a good correspondence to Curie-Weiss be-



Fig. 2. Temperature dependence of the dielectric constant of thiourea. Insert: $\epsilon'(T)$ by continuous plotting.



FIG. 3. Reciprocal dielectric constant as a function of temperature.

havior (Fig. 3), wherein $\epsilon' = B/T - T_c$, where B is a constant, and T_c is a characteristic temperature. The constant B has the value 2.84×10^4 /°K in Region I, and 3.7×10^3 /°K in Region V. The characteristic temperature in Region I is 169°K and in Region V, 185°K. The changes in the dielectric constant between Regions I and V are so rapid that it is not possible to establish with reliability a similar relationship over this temperature range.

Along the [100] and the [001] directions, the dielectric constant has a value of approximately 3 and shows only negligible variation over the entire temperature range from that of liquid nitrogen to room temperature.

C. Spontaneous Polarization and Ferroelectric Hysteresis

The apparatus employed for observation of hysteresis loops was a conventional Sawyer-Tower² loop tracer with a phase shifter for adjusting the relative phase of the horizontal and vertical signals. Among the various temperature ranges, hysteresis loops were observed only in Regions I and III, while in Regions II, IV, and V, linear D(E) characteristics were obtained. At high electric fields, double hysteresis loops are observed in Region II. This phenomenon, however, is associated with the characteristics of thiourea in Region I, as will be discussed, rather than with any characteristic of the Region II state.

The hysteresis loops observed in Region I are quite

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FIG. 4. Hysteresis loop of thiourea, 60 cps, $E_{\text{max}} = 785 \text{ v/cm}$.

² C. B. Sawyer and C. H. Tower, Phys. Rev. 35, 269 (1930).



FIG. 5. Spontaneous polarization as a function of temperature in Region I.

square and symmetrical (Fig. 4). The spontaneous polarization is approximately 3×10^{-6} coulombs/cm² and is relatively constant over the entire temperature range (Fig. 5). The temperature dependence is that characteristic of a ferroelectric exhibiting a first-order transition, the polarization dropping off abruptly at the transition point.

The coercive field at 60 cps and 140° K is 165 v/cm and behaves with temperature in a manner similar to that of the spontaneous polarization (Fig. 6). The coercive field in the immediate vicinity of the Curie point, however, appears to drop off more rapidly than does the spontaneous polarization. As a consequence, the hysteresis loops become extremely narrow immediately below the transition temperature, while their height remains essentially unchanged. This results at that temperature in a hysteresis loop which appears to have negligible coercivity. For this reason "low field" dielectric constant measurements at this point cannot be made. The frequency dependence of the coercive field was measured up to 100 kc, the maximum possible with our apparatus. Well-formed square loops are observed substantially throughout this range provided



graphite electrodes are used. There are frequencies in this range, however, at which there occur curiously distorted loops apparently because of piezoelectric resonances. The nature of the dependence of the coercive field on frequency was not determined because, with the Sawyer-Tower circuit employed, it was not possible to be certain that the signal was properly phased at the higher frequencies. It can be stated, however, that at 163°K the coercive field at 100 kc is no more than twice what it is at 60 cps.

As the temperature is raised above that of Region I into Region II, the hysteresis loops become double. This phenomenon was predicted by A. F. Devonshire³ to be characteristic of a first-order ferroelectric transition and was first observed by W. J. Merz⁴ in barium titanate. In a ferroelectric exhibiting a first-order transition, it was shown by Devonshire³ that the



FIG. 7. Double hysteresis loops above $(Tc)_{I}$.

transition temperature is a linear function of the electric field. At temperatures above the Curie temperature, therefore, the ferroelectric state can be produced by application of a suitably large electric field. When an alternating voltage is applied to the crystal in this temperature range, the crystal behaves as a normal linear dielectric until the voltage excursion produces a field sufficiently high to cause the material to become ferroelectric. At this point a hysteresis loop appears, giving rise to the double loop pattern (Fig. 7, one loop for each direction of the field). The predicted linear dependence of the transition temperature on field is illustrated in Fig. 8. The actual value of the Curie temperature has been deduced from this plot by adjusting the constant, T_c , so that the curve passes through the origin. This gives 168.4°K as the Curie

⁴ W. J. Merz, Phys. Rev. 87, 544 (1952).

³ A. F. Devonshire, Advances in Phys. 3, 85 (1954).



F10. 8. Dependence of I—II transition temperature on applied field. $E_0 =$ "zero" field coercive field, E = applied field, $T_c =$ transition temperature at "zero" field, and T = transition temperature at field E.

temperature, in good agreement with the value deduced from the spontaneous polarization and dielectric constant measurements. The temperature coefficient of the transition temperature is 1200 v/cm/°C as compared with a value 700 v/cm/°C found by Merz⁴ for BaTiO₃.

Aside from this double loop phenomenon, no other anomalies are found in Region II. As the temperature is raised further, however, into Region III, a second ferroelectric range is encountered also along [010]. The hysteresis loop is considerably smaller than that observed in Region I, giving a maximum spontaneous polarization corresponding to 2.5×10^{-9} coulomb/cm² (Fig. 9) and a very small coercive field (100 v/cm).

The temperature dependence of P_s in this range (Fig. 10) is reminiscent of that found in Rochelle salt, P_s falling to zero at two temperatures corresponding to an upper and a lower Curie temperature. In the case of thiourea in Region III, these temperatures are 173°K and 176°K. In view of the two Curie points it would be expected that two maxima in the dielectric constant would occur (cf. Sec. B) as in Rochelle salt. However, because of temperature instability in the apparatus, reliable observation of these maxima was not possible in the narrow temperature range of Region III, though they did appear to occur in some samples. The proximity of Region III to Region I makes it possible with large fields to produce a triple hysteresis loop, two loops corresponding to the transition temperature shift already mentioned, and the third to the Region III ferroelectricity. As the temperature is raised further, no additional hysteresis is encountered.

D. Pyroelectric and Piezoelectric Effect

In the temperature regions where linear dielectric properties obtain (Regions II, IV, and V), little knowl-



FIG. 9. Hysteresis loop of thiourea in Region III. $P_s \approx 2.5 \times 10^{-9}$ coulomb/ cm².

edge of the electrical state of the crystal can be derived from dielectric measurements alone. The x-ray structure studies to be discussed in detail indicate that in V the crystal may be considered to have an antiferroelectric configuration. These intermediate regions, however, have not yet been examined by diffraction techniques. The absence of hysteresis loops in IV plus the good correspondence to a Curie-Weiss relationship in V imply that the IV–V transition is from one antiferroelectric state to another. Alternatively, IV could correspond to a ferroelectric state of extremely high coercivity or essentially to a pyroelectric configuration. In order to gain further information regarding this temperature range and Region II as well, the pyroelectric and piezoelectric properties were examined.

According to Wyckoff and Corey⁵ and in agreement with our measurements, the room temperature struc-



FIG. 10. Temperature dependence of spontaneous polarization in Region III showing upper and lower Curie temperature.

ture of thiourea is orthorhombic with four molecules per unit cell and space group D_{2h}^{16} . In Region I, according to our measurements, the space group is orthorhombic C_{2v}^2 . Since at these two temperature extremes the crystal remains orthorhombic, it appears reasonable to assume that the intermediate states (II, III, and IV) also retain the orthorhombic structure. If this be the case, the only other available point group for the crystal is D_2 . Among these modifications, the holohedral form D_{2h} is centrosymmetrical and exhibits neither pyroelectricity nor piezoelectricity, while C_{2v} can exhibit both piezoelectricity and pyroelectricity, and D_2 , only piezoelectricity.

The pyroelectric behavior was examined by two techniques. One, a direct method, in which the charge released with a given incremental temperature change as a function of temperature was measured with an electrometer. The second method is a dynamic meas-

⁵ R. W. G. Wyckoff and R. D. Corey, Z. Krist. 81, 386 (1932).

urement, first reported by Chynoweth,⁶ in which a thermal increment is introduced by a pulse of white light, and the resulting charge release measured on an oscillograph. Both methods give similar results, but the latter proved to be substantially more convenient and reproducible. The results obtained by the pulse method are illustrated in Fig. 11. A small dc bias of a few volts/cm was applied to the crystal, while the pyroelectric measurements were being taken, to prevent antiparallel domain orientation which cancels the effect in the ferroelectric range.

The pyroelectric coefficient in IV and V is nearly zero except close to the IV–V transition, while over the remainder of the temperature interval studied it has a substantial value reaching a maximum at the I–II transition. It is apparent from the electrical measurements, therefore, that in Region IV the crystal is nonpolar and corresponds either to a paraelectric state or to an antiferroelectric state. The result in II is ambiguous since this region lies between two ferroelectric states which are very close to one another in temperature. As a consequence, the crystal is probably highly strained as the temperature passes through II, a condition which would give rise to pyroelectricity even in a centrosymmetric configuration.

Further information regarding the symmetry of the crystal in these intermediate regions is derived from an examination of the piezoelectric behavior. The frequency of the most conspicuous piezoelectric resonance was determined as a function of temperature by coupling a variable frequency oscillator to an oscillograph through a capacitor containing a cleavage plate of thiourea as its dielectric. A maximum in the signal







FIG. 12. Piezo resonance frequency as a function of temperature.

from the oscillator occurs at the frequency of resonance which is measured by a conventional frequency counter. In Fig. 12, the frequency of resonance as a function of temperature is plotted. Piezo resonance is observed throughout Region I, falling slowly in frequency as the transition temperature is approached. At the I–II transition, the resonance disappears and no further resonances can be found except for a very weak effect in III.

The absence of piezoelectricity in II, IV, and V, and the vanishing pyrocoefficient in IV and V lead to the conclusion that in all three ranges the crystal has no polar axis. The electrical measurements are consistent with two possible configurations, paraelectric and antiferroelectric, but general structural considerations make the antiferroelectric state far more probable.

E. Switching Behavior in Region I

If the direction of the spontaneous polarization of a ferroelectric crystal is reversed by the application of a fast-rising rectangular voltage pulse, the duration of which is much longer than the time required for domain reversal, the corresponding current pulse in a circuit external to the crystal gives an indication of the manner in which ferroelectric domains reverse. The schematic diagram of a typical experiment together with the appropriate wave forms is illustrated in Fig. 13.

In our experiment the voltage pulse is generated by a pair of mercury relays⁷ designed to give single pulses of either polarity and of a wide range of duration and amplitudes. The peak currents drawn in the shorter pulses are of the order of 1 amp, and hence a lowimpedance voltage source is essential. In our case, the

⁷ J. R. Anderson (private communication).



FIG. 13. Measurement of switching time in ferroelectrics.

voltage was derived from batteries. Rise times of the order of 10^{-8} sec are achieved with this pulse generator. Curve (a) in Fig. 13 represents the applied voltage pulse. A typical switching pulse observed when polarization is reversed is shown in curve (b). The switching current (i_s) is defined as the value at the peak of the switching curve and the switching time (t_s) , the total duration of the switching curve. The quantities i_s and t_s are inversely proportional to one another so long as the shape of the switching curve remains unchanged. When a second pulse of the same polarity as the first is applied, no switching takes place, and the current pulse represents only the charge transferred by the shunting capacitance and by the residual capacitance of the ferroelectric. This is illustrated in curve (c).

Switching curves for thiourea at two extreme values of voltage pulse amplitude are shown in Fig. 14. At high fields [Fig. 14(a)], the pulse has a simple shape similar to that of Figure 13(b). The irregularities in the rising portion of the curve are oscillations in the applied pulse. In this case, the switching time is 7×10^{-7} sec. At low fields, the pulse develops a more irregular contour which is the result of individual domains slowly reversing. The total charge transferred, as



measured on an electrometer, is the same for both extreme values of applied field, and it corresponds to twice the spontaneous polarization as derived from the hysteresis loop. The relation between switching time and applied field is plotted in Fig. 15 as $\log t_s$ vs E at 150°K over the field interval from 50 v/cm to 4000 v/cm. These limits were established at the low-field end by uncertainties in switching time produced by Barkhausen noise in the switching pulse, and at the high field end by limitations in the speed of response of the electronics. Between fields of 100 v/cm and 3000 v/cm, the switching time is proportional to $E^{-\frac{3}{2}}$, while at lower fields it deviates significantly from this relationship. At the low-field end, the data fit an exponential law of the type $t = t_0^{\alpha' E}$ where $t_0 = 10^{-4}$ sec and $\alpha = 2.7 \times 10^2$ v/cm (Fig. 16).

A detailed study of similar switching characteristics in BaTiO₃ has been reported by Merz⁸ who found that the switching current in BaTiO₃, at high values of applied field, is a linear function of field, while at low fields the relationship is exponential of the type $i_s \sim e^{\alpha/E}$ where α is a temperature-dependent constant. His measurements gave good correspondence to this relationship over five orders of magnitude in current with a value of the order of 10^4 v/cm. These results are considerably different from analogous measurements in ferromagnetic materials in that they indicate the absence of a true "coercivity" since a ferroelectric evidently will switch at an arbitrarily small value of applied field, given sufficient time.

It was indicated by Merz that the origin of this exponential behavior at low fields is in the limited sidewise domain wall motion with the corresponding requirement that many domains must nucleate before the polarization is reversed. At low fields this nucleation time dominates, and we obtain an "activation field" for domain nucleation. At higher fields, the polarization reversal is limited in rate by domain wall mobility which results in a linear relationship between field and switching current.

In the measurements on thiourea, it was found more desirable to consider the switching time rather than

⁸ W. J. Merz, Phys. Rev. 95, 690 (1954).

switching currents because of the irregular shape of the switching curve at low fields. It is reasonable, however, to assume corresponding relationships for i_s and t_s . In the low-field region, thiourea and BaTiO₃ exhibit similar behavior, both adhering to an exponential relationship. The range over which the exponential law obtains for thiourea is significantly less than for BaTiO₃, and the "activation field" is substantially lower, 10² v/cm as opposed to 10⁴ v/cm in BaTiO₃. This difference in "activation field" and the short range for exponential behavior imply either that domains in thiourea are far easier to nucleate or that fewer nuclei are required to produce reversal of the polarization. If the latter alternative is correct, then one must assume considerable sidewise nucleus wall motion on switching.

In the high-field region, the linear relationship between inverse switching time and field observed in BaTiO₃ is not found but rather a $\frac{3}{2}$ -power law obtains. The linear dependence of inverse switching time with field is explained by Merz on the basis of negligible sidewise domain wall motion with a consequent growth primarily in the direction of the field. This conclusion also indicates that the driving force for the new domain walls is always proportional to the applied field. In the case of thiourea, the field dependence is greater than linear. It is conceivable that the restricted field range over which this can be observed constitutes a region of transition between exponential and linear



FIG. 15. Log switching time vs log field.



and that measurements at higher fields would yield a linear relationship. Alternatively, the presence of space charge in the crystal could result in a driving field which is not linearly dependent on the externally applied field, giving rise to the $-\frac{3}{2}$ -power law. (Recent measurements on BaTiO₃ at high fields by Stadler⁹ exhibit a similar 1.5-power relationship.) Further study of the behavior of the thiourea domains is required before these alternatives can be resolved.

F. Deuterated Thiourea

In most ferroelectric materials containing hydrogen, hydrogen bonding plays a significant role in the ferroelectric mechanism (e.g., KH_2PO_4). As a consequence, isotopic substitution of deuterium for hydrogen results in substantial changes in the transition temperature and in other ferroelectric properties. A well-known example of this effect is in KH_2PO_4 , where the Curie temperature shifts from 123°K to 213°K upon substitution of D for H.¹⁰ It is unlikely that hydrogen bonding occurs in thiourea crystals since hydrogen bonds involving sulfur are at best doubtful. Further, the bond distances as deduced from structure studies are larger than would be reasonable for hydrogen bonding. It was decided, however, to explore this speculation

⁹ H. L. Stadler, J. Appl. Phys. 29, 1485 (1958).

¹⁰ Stephenson, Corbella, and Russel, J. Chem. Phys. 21, 1110 (1953).



FIG. 17. Dependence of dielectric constant on temperature in deuterated thiourea.

further by preparing crystals of deuterated thiourea and comparing the electrical properties with those of the undeuterated form. Deuterium was introduced into thiourea by recrystallization several times from heavy water.¹¹

The crystallites were dried, redissolved in CH₃OD (prepared by reacting heavy water with NaOCH₃) and large crystals grown by slowly lowering the temperature.³ Mass spectrometric measurements indicated that 93% of the hydrogen in the resulting crystals was replaced by deuterium. Cleavage plates were prepared for measurement by electroding with evaporated gold.

In general, the properties of the deuterated thiourea were not significantly different from those of the normal variety. The spontaneous polarization, dielectric constant, and coercive field showed negligible changes. The temperature dependence of the dielectric constant, however, does show significant changes (Fig. 17), the three major anomalies being shifted upward in temperature by 16°C, 16°C, and 11°C, respectively. In addition, the small inflection between I and II in the case of the normal compound is considerably more pronounced indicating that a fourth anomaly does occur at that point.

The relatively small change in the dielectric properties between normal thiourea and the deuterated modification tend to confirm the contention that proton motion alone does not account for the ferroelectric behavior. It appears, rather, that the only effect of isotopic substitution is in the dipole moment of the molecule as a whole and that this change is relatively small. A small upward shift in the transition temperature is consistent with the increase of mass of the molecule with a corresponding decrease in vibrational energy at any given temperature.

III. CRYSTAL STRUCTURE

Thiourea was one of the earliest organic crystal structures to be investigated. Wyckoff and Corey⁵ found that at room temperature the crystals belong to the orthorhombic centrosymmetric space group $D_{2\hbar}^{16}$ with four molecules per unit cell. The asymmetric crystal unit consists of half of one molecule, the carbon and sulfur atoms lying in the mirror plane, and the molecule was found to be planar within experimental error. No hydrogen bonding was found. A very recent three-dimensional analysis by Kunchur and Truter¹² has confirmed these results. The molecule, excluding hydrogen atoms, was shown to be very precisely planar and the intermolecular distances were found to be greater than normal van der Waals approaches. In addition, accurate bond distances and anisotropic thermal vibrations for all the atoms were given. The hydrogen atoms could not be observed presumably because of large thermal motion. In order to investigate the ferroelectric transition in thiourea, we have carried out a two-dimensional x-ray structure analysis of thiourea crystals at 120°K (Region I). This temperature is lower than the lowest and greatest dielectric anomaly already described, and consequently an accurate picture has been obtained of the crystals in the ferroelectric state. Oscillation and back reflection Laue photographs revealed that the orthorhombic symmetry was maintained at the lower temperature. The hk0 reflections occurred only with keven, as at room temperature, and therefore the lowtemperature phase also had a glide plane parallel to b. However, hol reflections with h+k odd occurred, very weakly for the low-angle reflections, but quite strongly at high angles, 700 and 701 being outstanding. Thus, the centering of the *b*-axis projection and hence the diagonal glide plane was destroyed on cooling.

The observed systematic extinctions could arise from two formally possible space groups, C_{2v}^2 and $C_{2\nu}^4$. The second, however, could be ruled out as a structure based on this space group could not possibly be arrived at by any small movement from the room temperature structure. The broad intensity distribution, the fact that the crystals very rarely shattered on cooling, and the ferroelectric reversal itself made C_{2v}^2 the only reasonable space group. The reduction from 8-fold to 4-fold symmetry of the general positions is accomplished by a doubling of the crystal asymmetric unit from one half molecule to two halves of two molecules, now having certain independent crystallographic degrees of freedom. The mirror plane perpendicular to the molecular plane is still in existence in both molecules.

Consideration of the h0l intensity data showed clearly

¹² N. R. Kunchur and M. R. Truter, J. Chem. Soc. 1958, 2551.

¹¹ The authors are indebted to R. Schaufele for working out this procedure and for growing the crystals.

that the positional changes involved in the transition were much greater in the x direction than in the z. The Patterson projection showed a sulfur-sulfur vector at about 0.47a, 0.5b. A simple structural change which would account for these facts could immediately be postulated. If the pair of molecules related by the b-axis glide plane (Fig. 19) and centered at 0,0 were mutually translated along a by a small amount and if the pair centered at a/2, c/2 had relative translations of opposite sign to the first pair, i.e., so that one pair overlaps more than at room temperature, the other less, then the projection centering would be broken in the manner indicated. The first refinement on this basis showed that the independent molecules had different tilts with respect to the b axis and as refinement progressed, it became clear that this was a more important effect than the translational one in accounting for the change in atomic positions.

TABLE I. Coordinates of the atoms.

	Molecule A			Molecule B			
	x	У	z		x	у	Z
$\begin{array}{c} & \\ S_1 \\ C_1 \\ N_1 \\ H_1 \\ H_2 \end{array}$	$\begin{array}{r} 0.349 \\ 0.049 \\ -0.071 \\ -0.244 \\ 0.016 \end{array}$	$\begin{array}{r} -0.003\\ 0.075\\ 0.105\\ 0.150\\ 0.082\end{array}$	0.000 0.000 0.135 0.135 0.238	${f S_2} \\ {f C_2} \\ {f N_2} \\ {f H_3} \\ {f H_4}$	$\begin{array}{r} 0.125 \\ 0.399 \\ -0.491 \\ -0.332 \\ 0.429 \end{array}$	$\begin{array}{r} 0.010 \\ -0.103 \\ -0.149 \\ -0.215 \\ -0.115 \end{array}$	0.500 0.500 0.365 0.365 0.262

A. Crystal Data at 120°K

Thiourea CS(NH₂)₂ mol. wt., 76.11; *d* calc, 1.438; orthorhombic pyramidal, $a=5.494\pm.005$, $b=7.516\pm$ $\pm.007$, $c=8.519\pm.010$ A; Absent spectra, *hk*0 when *k* is odd; Space group C_{2v}², four molecules per unit cell; Molecular symmetry, plane, volume of the unit cell, 351.8 A³; Absorption coefficient for x-rays (λ =1.5405 A), μ =60.9/cm; Total number of electrons per unit cell=F(000) = 160.

B. Refinement of the Structure

Refinement of the postulated structure was carried out by Fourier series methods for the three principal projections. Initially ρ obs series were calculated and in the later stages both ρ obs and ρ obs- ρ calc series were used. Altogether, 20 two-dimensional series were calculated on the IBM 650 computer. In all cases the aaxis was divided into 30 parts, the b and c axes into 60 parts, giving intervals of 0.183 A, 0.125 A, and 0.142 A, respectively. The maps were prepared by linear interpolation and the atomic centers found by drawing several graphs through each atom. Back shift corrections for termination of series errors were applied using 1.0 (Δx , Δy , Δz) for the centrosymmetric hol projection and 1.5 (Δx , Δy , Δz) for the noncentrosymmetric 0kl and hk0 projections. The final atomic positions obtained are listed in Table I and the three



FIG. 18. The electron density map of the projection on (100). Contours are drawn at intervals of 2 electrons/ A^2 starting at the dotted 2 electron line for the nitrogen and carbon atoms. For the sulfur atoms the contours are 2 (dotted), 4, 8, 12, etc., electrons/ A^2 . In this and succeeding diagrams, the sulfur, carbon, and nitrogen atoms of each molecule are connected by full lines while the probable coplanar hydrogen atom positions are joined to the nitrogens by dotted lines.

final ρ obs maps are shown in Figs. 18, 19, and 20, with the molecular skeleton superposed.

The coordinate refinement was entirely isotropic and one temperature factor with B=2.4 was used for all atoms. While the difference maps indicated a rather larger temperature factor for nitrogen than for sulfur, trials with different values of B for each atom resulted in no over-all improvement in the agreement factor. Since it was considered desirable to keep to a minimum the number of parameters being refined with limited data, no change was made. However, the use of an anisotropic temperature factor seemed to effect a real



FIG. 19. The electron density map of the projection on (010). Contours as in FIG. 18.



FIG. 20. The electron density map of the projection on (001). Contours are drawn at 3 (dotted), 6, 8, 10, etc., electrons/A² for the nitrogen and carbon atoms and at 3 (dotted), 6, 10, 14, etc., electrons/A² for the sulfur atoms.

improvement. By trial from the final coordinates, it was found that the best agreement with the observed data could be obtained by using a temperature factor of the form $\exp((A + B \cos^2 \phi)) (\sin \theta / \lambda)^2$ where ϕ is the angle between the reciprocal lattice point hkl and b^* , with A = 1.7 and B = 1.5. This has been included in the F calc column of Table II which lists the observed and calculated structure factors and the final calculated phase angles for the three zones investigated. The Rfactor for all observed reflections, defined as $R=\Sigma$ $(|F \text{ obs}| - |F \text{ calc}|) / \Sigma F \text{ obs was } 0.140 \text{ with the iso-}$ tropic temperature factor and 0.122 with the anisotropic temperature factor, both without hydrogen atoms. Inclusion of the hydrogen atoms in the positions given in Table I which are discussed later, brought a further reduction to 0.109.

C. Dimensions of the Molecule

The bond distances and bond angles obtained from the final coordinates are collected in Table III. The differences between the dimensions of molecule A and molecule B now environmentally different, cannot be regarded as significant but rather are indicative of the magnitude of experimental error to be expected from two-dimensional work with visual x-ray intensities. The carbon position is found to be almost exactly in the plane of the sulfur and nitrogen atoms in both molecules. Owing to the lack of resolution in all but one projection, however, the carbon coordinates must be regarded as the least certain. What the experimental results show is that if any deviation from planarity of the carbon, nitrogen, and sulfur atoms of either molecule occurs, it must be a very small one.

It is of interest to compare the results recently obtained by Kunchur and Truter¹² for the thiourea molecule at room temperature with three-dimensional data (177 observed reflections and 7 positional parameters) with those obtained from the present work with data from only the three principal zones (127 observed reflections and 14 positional parameters). The only appreciable deviation from the results given in Table III is in the C-S bond which was measured by Kunchur and Truter as $1.71 \pm .01$ A, as against our mean value in the two molecules of 1.74 A. Since this last value can hardly have a maximum possible error of less than ± 0.02 A, it can be said that the dimensions of the thiourea molecule, excluding hydrogen atoms, are identical within the limits of the experimental observations with those found at room temperature.

D. Hydrogen Atoms

The x-ray scattering power of four hydrogen atoms as against that of one sulfur, one carbon, and two nitrogen atoms is so small even for atoms at rest, that only the most precise x-ray work could be expected to give definite information about their positions. In the present work, based on projections only, the number of reflections to which the hydrogens could make appreciable contributions is extremely small. It is hardly surprising, therefore, that nonoverlapping hydrogen atoms are represented in the electron density and difference maps by peaks little higher than the random background fluctuations. However, in the most probable configuration of the hydrogen atoms, coplanar with the rest of the molecule as found in urea,¹³ there is a near overlap in the h0l projection of two hydrogen atoms (H₂ and H₄) with the glide-plane related pair, and in the hk0 projection all four crystallographically independent atoms are exactly superposed on their images across the mirror plane.

Figure 21 shows the final ρ obs- ρ calc map for the *b*-axis projection. The two strongest peaks correspond rather exactly to the residual density which would be expected from H₂ and H₄ closely overlapping their symmetrically related pair. These peaks are also strong in the ρ obs map (Fig. 19). H₁ and H₃ which do not overlap with any other hydrogen atoms, are represented by weak peaks which are weaker than the apparently spurious peak at a/2, c/6. In Fig. 22 the corresponding map for the *c*-axis projection is shown. In this calculation the anisotropic temperature factor was included in the calculated structure factors subtracted out since in the "isotropic" map previously

¹³ Worsham, Levy, and Peterson, Acta Cryst. 9, 754 (1956).

TABLE II. Observed and calculated values of the structure factors and final calculated phase angles.

hkl	F obs	F calc	a calc	hkl	F obs	F calc	a calc
002	51	56	0	303	17	17	0
004	20	19	0	304	15	13	0
006	44 34	40	0	305	18	18	0
00, 10	14	13	ŏ	307	20	21	ŏ
020	51	51	0	308	<2	1	•••
040	7	6	0	309	15	14	0
080	19	13	ŏ	401	27	24	180
100	<1	2		403	11	13	0
200	28	27	0	404	24	24	180
300 400	19	19	180	405	18	15	180
500	13	14	180	407	$\overline{<2}$	1	
600	4	5	0	408	11	14	180
021	38	38	180	501	3	0 4	180
022	44	46	1	503	ž	$\overline{3}$	Ő
023	23	19	256	504	4	4	0
024	33	38	259	505 506	5	3 6	180
026	29	26	205	507	3	3	Ő
027	11	15	76	601	4	2	0
028	19	19	2 77	603	4 14	4 14	0
02, 10	13	14	1	604	4	4	ŏ
041	<2	1		605	10	9	0
042	29	29	4 8	110	34	38	180
044	33	33	353	210	14	11	290
045	2	2	353	310	17	13	78
040 047	15	14	20	410	22	18	00 272
048	28	8	44	610	$\tilde{<2}$	2	
049	<2	1		710	4	3	212
04, 10	13	11	359 243	220	48	51 5	236
062	18	15	17	320	13	14	52
063	7	6	7	420	24	24	201
064	13	12	24 322	520 620	6 < 2	6	197
066	6	11	18	130	32	32	76
067	7	8	239	230	4	5	118
068	7 7	8	17 261	330	11	17	69 76
082	10	9	16	530	16	11	277
083	7	5	105	630	5	4	296
084	11	9 4	44 256	140	10	8 21	68 150
086	6	8	1	340	6	$-\frac{1}{7}$	329
101	13	10	0	440	18	18	173
102	5 41	43	180	640	7	7	251
104	4	5	0	150	19	18	101
105	21	22	180	250	6 11	10	131
106	<2<2	2	•••	450	8	9	105
108	$\langle \tilde{2}$	ĩ		550	7	9	246
109	3	4	180	160	95	9	211
201	2 9	10	180	360	5	6	240
202	5	7	180	460	8	7	175
203	<2	1	180	560	7 11	6 10	182 116
204	<2	19		270	5	5	183
206	<2	3		370	8	7	147
207	2	4	180	470	<2	3	263
208	4 3	2	180	180	<2	1	203
20, 10	3	3	180	280	8	4	265
301	36	36	0	190	5	5	104
	J	0					

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Molecule A		Molecule B	
S—C	1.748	1.72,	
C—N	1.343	1.34_{0}	
S-C-N	121.1°	120.9°	
N-C-N	117.8°	118.2°	

TABLE III. Bond distances and angles.

calculated the density from this cause interfered with some of the hydrogen peaks. There are only seven peaks of height greater than 1 electron A² and three of these, including the two strongest, agree very well with the expected positions for H_1 , H_2 , and H_4 . The third strongest peak in the map is close to the expected position for H_3 but is large in area and its center is about 0.5 A from the H₃ position. Comparison with the ρ obs map suggests that the highest part of this very elongated peak is due to resultant false diffraction effects of the adjacent sulfur, carbon, and nitrogen atoms, which have been incompletely subtracted. However, we have seen that the expected position for this atom was in remarkable agreement with the observed density in the h0l maps which are probably more reliable because they are centrosymmetric and also since the peak is further away from any residual diffraction effects. In such an overlapping projection as the hk0, very precise thermal parameters would be required for a complete subtraction.

If the two difference projections are taken together,



FIG. 21. The pobs-pcalc map for the (010) projection. Contours are at intervals of $\frac{1}{2}$ electron/A² starting at the 1 electron level.



FIG. 22. The ρ obs- ρ calc map for the (001) projection. Contours as in FIG. 21.

it would seem that the evidence for the hydrogen atoms being at least approximately coplanar with the rest of the molecule is quite strong.

E. Intermolecular Distances and Packing

The shortest distances between nitrogen and sulfur atoms, and between two nitrogen atoms, in different molecules are shown in Table IV. The dashed atoms are those related to the standard atoms listed in Table I by the operation \bar{x} , $\frac{1}{2} + y$, z. Translations from either position are shown in brackets. No intermolecular distance is shorter than the normal van der Waals distance and hydrogen bonding can be ruled out, even

TABLE IV. Intermolecular	approaches in	thiourea.
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	Low temperature distance (A)	Room temperature distance (A)
S_1N_2	3.41	3,42
S_2N_1	3.37	3.42
$S_1 N_1 (+a)$	3.49	3.70
$N_2S_2(+a)$	3.87	3.70
$S_1 N_2 (+a)$	4.17	4.31
$S_2 N_1'(-b)$	4.37	4.31
$S_1 N_1 (-b)$	3.51	3.51
$S_2 N_2'(+a)$	3.45	3.51
$N_1 N_1'$	3.83	3.84
$N_2N_2'(+a)$	3.76	3.84
$N_2 N_1'(+a-b)$	4.11	3.89
$N_2 N_1'(-b)$	3.62	3.89
N_2N_1	4.20	4.32
$N_2 N_1 (+a)$	3.59	3.79

without consideration of the hydrogen atom positions already discussed. While there is a comparatively large change in the orientation of the molecules (the room temperature angle of 63.6° between the normal to the molecular plane and [010] becomes 70.6° for molecule A and 60.5° for molecule B), the changes in intermolecular distances seem to be extremely small.

F. Experimental

The crystals used had been grown from methanol as described and were cut down to suitable size for x-ray investigation. The crystals for the *a*-, *b*-, and *c*-axis measurements had mean diameters of 0.24 mm, 0.35 mm, and 0.22 mm, respectively. The variation between the maximum and minimum diameters in each specimen was not greater than 10%.

The crystals were mounted on glass fibers sealed in an insulating lava base. Cooling was accomplished by the now standard technique of passing dried helium gas through liquid nitrogen and then through the central tube of a double-walled Dewar column, mounted about 1 cm above the crystal. Dried air at room temperature passed through a concentric annular space surrounding the central tube served to prevent icing. Temperature control could be achieved by changing the proportions of the air and helium flow. Temperatures were measured by a copper-constantan thermocouple, mounted either touching or very close to the base of the crystal.

The x-ray measurements were made with $CuK\alpha$ radiation, by using rotation and oscillation photographs and the multiple film technique. For greater uniformity, the complete rotation photographs were used for the intensities of as many reflections as could be resolved and the oscillations only for very weak and unresolved reflections. Intensities were estimated visually with the aid of a time calibrated scale and Lorentz, polarization, and cylindrical absorption corrections applied.

For accurate measurement of the unit cell dimensions, back reflections were recorded from the a, b, and c faces of crystals mounted on a goniometer designed for use in conjunction with the Norelco diffractometer.

IV. DISCUSSION

The unit cell of thiourea crystals at room temperature contains four molecular dipoles whose components resolved in any crystallographic direction, cancel each other, resulting in a nonpolar crystal. Under the usual definition as applied to ionic crystals,¹⁴ this would be considered an antiferroelectric arrangement. At temperatures below 169°K, the crystals exhibit ferroelectric properties. In this temperature range, the electrical and x-ray studies have given us a fairly clear picture of the crystal structure and of the mechanism of the ferroelectric reversal. Viewed in the direction of the crystal c axis, the low-temperature structure consists

¹⁴ C. Kittel, Phys. Rev. 82, 729 (1951).

Fig. 23. An illustration of the ferroelectric reversal in thoi

FIG. 23. An illustration of the ferroelectric reversal in thoiurea projected on (001). The full circles represent atomic positions for one direction of the applied field; the dotted circles represent the new atomic positions on reversal of the field.

of two nonequivalent pairs of molecules whose tilts with respect to the crystal b axis are appreciably different. Consequently, dipole components in the [010] direction do not cancel and the crystal has a pyroelectric axis. By analogy with the magnetic case, in this temperature range the material could be said to be ferrielectric. This projection of the crystal structure is shown in Fig. 23. The full circles represent the atomic positions in one polar configuration and the dotted circles, the atomic positions in the reversed configuration. While the atomic movements required to reverse the structure are fairly large (about 0.5 A for the nitrogen atoms), the direction of movement is close to that of the largest thermal vibrations. It is, therefore, easily understandable that a reversal of polarization can occur under a relatively small driving field. As a consequence, this material is a ferroelectric with low coercive field and fast switching. Its ferroelectric behavior is similar to that of known ferroelectrics with first-order transitions.

The minor dielectric anomalies described above are not yet clearly understood. It is probable that they are due to smaller relative displacements of the molecules. The substitution of deuterium for hydrogen in the crystal results in small but significant changes in the transition temperatures. Consequently, it is apparent that the protons are not in themselves the major factor in the mechanism, although their positions and thermal motion may be of importance in determining the molecular packing.

We are indebted to A. Kalantar for preparing the crystals of thiourea used in this work and for making certain electrical measurements, to R. W. Easton and M. M. Hopkins for assistance in the electrical studies, and to Mrs. H. Kulsrud and Mrs. D. Garrison for carrying out the numerical computations in the crystal structure analysis.