Dielectric and neutron diffraction studies of radiation damage on modulated deuterated thiourea $[SC(ND_2)_2]$

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In order to demonstrate the effect of x-radiation damage on a typical modulated insulator, dielectric susceptibility and neutron diffraction measurements were performed on previously irradiated specimens of deuterated thiourea $[SC(ND_2)_2]$. With increasing irradiation dose, an enhancement of hysteresis and memory effects is observed, together with a smearing out of the lock-in phases of order 9 and 8. Neutron measurements of the modulation wave vector $\delta\mathbf{b}^*$ give evidence for the existence of quasiplateaus in the $\delta(T)$ curve for irradiated samples. The connection between the present findings and results from a previous x-ray study on $SC(ND_2)_2$ in an applied electric field is discussed.

I. INTRODUCTION

Thiourea is a well-known molecular modulated insulator characterized by a frozen electric polarization wave with propagation vector $\mathbf{q}_\delta=\delta\mathbf{b}^*$. Most of the current interest in this compound is associated with the response of the modulation to external parameters: temperature T, pressure P, and electric field E (for a review see Ref. 1). In particular, locked phases of commensurability orders 9, 7, and 3 have been observed in a neutron diffraction study of the (P,T) phase diagram,[2–4] while the existence of a commensurate phase of order 8 under an applied electric field, has been predicted[4] and confirmed experimentally.[5–7]

In a recent x-ray study,[8] new field-induced commensurate phases with unusually high commensurability order, such as $\frac{2}{15}$, $\frac{4}{29}$, and $\frac{6}{43}$, have been reported at large applied fields. The wide stability range of these new commensurate phases (5—15 K) was interpreted in terms of *intrinsic* lattice discreteness effects.

In contrast, macroscopic techniques, such as optical birefringence and dielectric susceptibility measurements[9] have failed to detect any anomalies at high fields, except for those associated with the commensurate phase of order 8. Figure 1 shows a sketch of the (E,T) phase diagram as obtained from the position of birefringence anomalies.[9]

A subsequent neutron diffraction study[7] at large fields ($E=0.5$, 1.2, and 1.8 kV/mm) showed a *smooth* behavior for $\mathbf{q}_\delta(E,T)$, with a single plateau at $\delta=\frac{1}{8}$.

In order to account for the strong discrepancy between the x-ray work in Ref. 8 and the neutron diffraction results[7] the suggestion was made that radiation damage from the x-ray beam itself could affect the x-ray results. This last hypothesis was at least partly supported by neutron diffraction data[7] on an x-ray irradiated specimen, showing a shift of the $\mathbf{q}_\delta(T;E=0)$ curve by about 2 K downwards. However, the curve remained smooth, with no indication for additional steps or discontinuities, at least within the (limited) temperature range of the experiment.

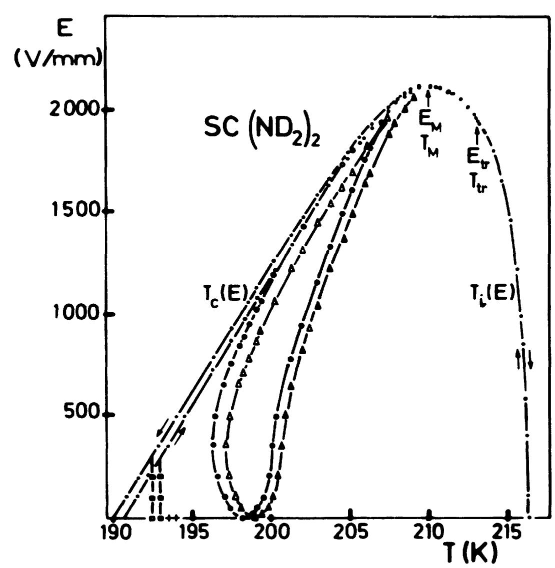

FIG. 1. (E,T) phase diagram for increasing and decreasing temperatures. The boundaries of the commensurate $\delta=\frac{1}{8}$ phase are shown as triangles ($T\uparrow$) or circles ($T\downarrow$). The triangular region in the lower left corner of the figure corresponds to $\delta=\frac{1}{9}$ (after Ref. 9).

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The present paper reports on dielectric susceptibility and further neutron diffraction measurements on $SC(ND_2)_2$ specimens which have been x-ray irradiated under carefully controlled experimental conditions. In each case, the behavior of ϵ_a and $\mathbf{q}_\delta$ has been followed over a wide temperature range and for several values of the applied bias field (Secs. II and III). The results show that irreversible effects (hysteresis, memory effects) are enhanced in the irradiated samples, while the commensurate plateaus at $\delta=\frac{1}{9}$ and $\frac{1}{8}$ are smeared out. In addition, several quasiplateaus are observed on the $\mathbf{q}_\delta(T)$ curve, both with and *without* applied field. The position of the plateaus does not appear to be related to any simple rational value of δ. A qualitative discussion of these results in terms of pinning and unpinning of the modulation by mobile defects is presented in Secs. III and IV.

II. DIELECTRIC MEASUREMENTS

A. Experimental method

Thin single-crystal plates of deuterated thiourea were cleaved from a large sample. The cleaved faces are normal to the a axis of the orthorhombic *Pnma* structure. Each plate is irradiated at room temperature using the unfiltered radiation from a conventional molybdenum-target x-ray tube operated at 40 kV (irradiation rate: 0.8 Mrad/hour).

Following irradiation, the cleaved faces are metallized by vacuum deposition (Cr + Au films). Gold leads fixed with a Pt-based lacquer are used as electrodes. The dielectric constant is measured with an automatic Hewlett-Packard 4275-A *LCR*-meter, at a frequency of 10 kHz. Measurements are performed as a function of temperature for fixed values of the bias field.

Because of the *mobility* of the defects created by irradiation, it is important to specify the time scale of the measurements. In the present case, the data were taken point by point at an approximate rate of one point every 6 min corresponding to the time required to change and stabilize the specimen temperature to within ± 0.02 K of the set point.

B. Results ($E=0$)

Figure 2(a) shows a typical plot of ϵ_a', the real part of the complex dielectric function in the a direction, as measured on a virgin sample, in zero-bias field. The main features in Fig. 2(a) have already been described:[1,10] The stability range of the modulated phases is bounded, on the high-temperature side, by a cusplike anomaly at the second-order modulated-to-paraelectric transition T_i, and by a sharp spike, on the low-temperature side, corresponding to the first-order modulated-to-ferroelectric transition T_c. The anomalies observed inside the modulated region, at T_1, T_2, and T_3 have been assigned, on the basis of neutron diffraction data, either to a lock-in transition at the commensurate value $\delta=\frac{1}{9}$ ($T=T_1$) or to the passage of the modulation wave vector through the commensurate values $\delta=\frac{1}{8}$ ($T=T_2$) or $\delta=\frac{2}{17}$ ($T=T_3$). The magnitude of the anomaly at T_2 reflects the ferroelectric character of

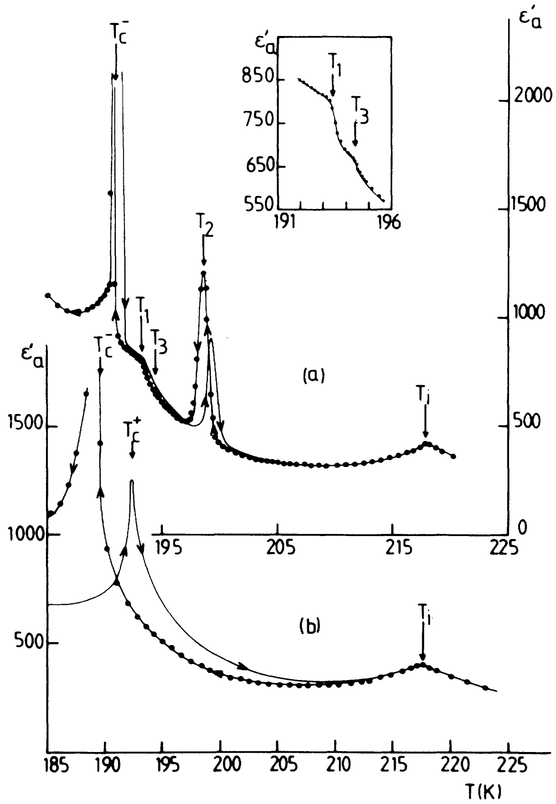

FIG. 2. The real part of the dielectric function, $\epsilon_a'(T)$, as measured on a virgin sample (a) and after a 90-Mrad x-ray exposure (b).

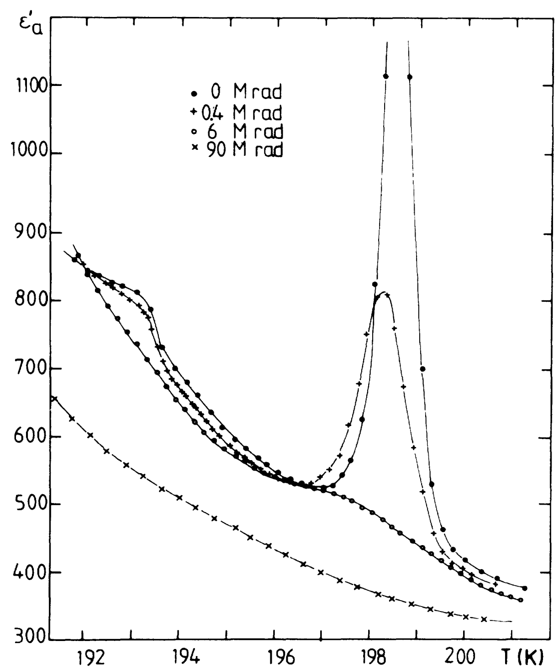

FIG. 3. The real part of the dielectric function, $\epsilon_a'(T)$, as a function of radiation dose: (●) 0 Mrad; (+) 0.4 Mrad; (○) 6 Mrad; (×) 90 Mrad.

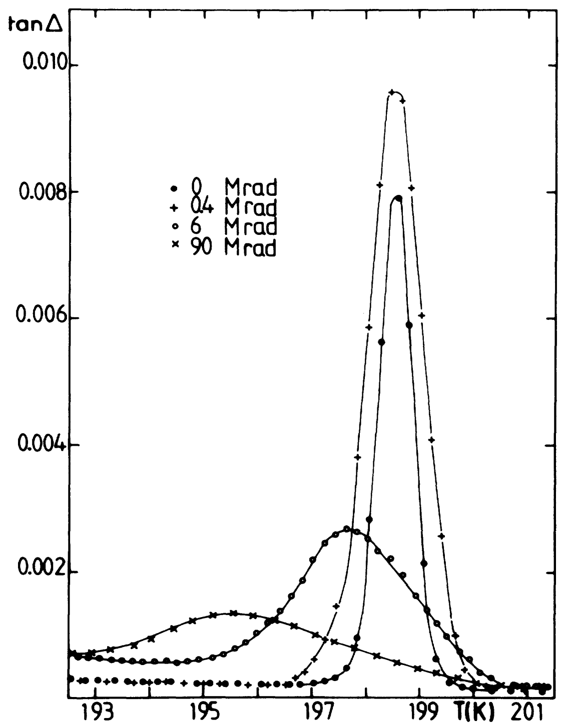

FIG. 4. Dielectric loss ($\tan\Delta = \epsilon_a''/\epsilon_a'$) as a function of radiation dose. The various symbols have the same meaning as in Fig. 3. All measurements were performed with an ac-field amplitude of ± 0.1 V/mm.

the incipient $\delta = \frac{1}{8}$ phase. A small hysteresis is observed throughout the modulated region ("global hysteresis"), with vanishing amplitude in the limit $T \rightarrow T_i$.

The effects of radiation damage are illustrated in Fig. 2(b), which shows ϵ_a' for an irradiated specimen with an accumulated dose of 90 Mrad. The main differences with Fig. 2(a) are the following: (i) the enhancement of the amplitude of the thermal hysteresis and (ii) the absence of dielectric anomalies associated with commensurate values of δ, inside the modulated region ($T = T_1, T_2, T_3$).

Part of the same data is plotted on a larger scale in Fig. 3, together with data from less-irradiated samples (0.4 and 6 Mrad). The corresponding loss factors, defined by $\tan\Delta = \epsilon_a''/\epsilon_a'$ (ϵ_a'' is the imaginary part of the complex dielectric function) are shown in Fig. 4. Obviously the strength of the anomalies at T_1 and T_2 is very sensitive to radiation damage: for example, the 6-Mrad sample shows no anomaly at T_1 and the peak at T_2 is considerably smeared and shifted to lower temperatures. This last point is seen very clearly in the loss factor data in Fig. 4.

C. Results ($E \neq 0$) and discussion

The first question raised by the above results concerns the character of the modulated state in the presence of radiation damage: Are the irradiated samples long-range ordered, in the sense of the modulation periodicity $\mathbf{q}_\delta$ remaining sharply defined? Although this point is more aptly discussed in the light of diffraction data (cf. Sec. III E), we remark that the anomalies at T_i, T_c^+, and T_c^- remain sharp on the irradiated samples [cf. Fig. 2(b)], which would appear to indicate that the long-range-ordered character of the modulation is largely preserved.

The smearing and eventually the vanishing of the anomalies at T_1 and T_2 raise a second question, about the stability of the $\frac{1}{8}$ and $\frac{1}{9}$ commensurate phases in the presence of irradiation defects. As far as the $\frac{1}{8}$ phase is concerned, useful information can be extracted from dielectric measurements at finite electric fields. As is known from previous measurements on virgin samples,[11] the effect of a small bias field is to split the T_2 anomaly into two separate peaks corresponding to the stability limits of the $\frac{1}{8}$ phase. The amplitude of the two peaks decreases

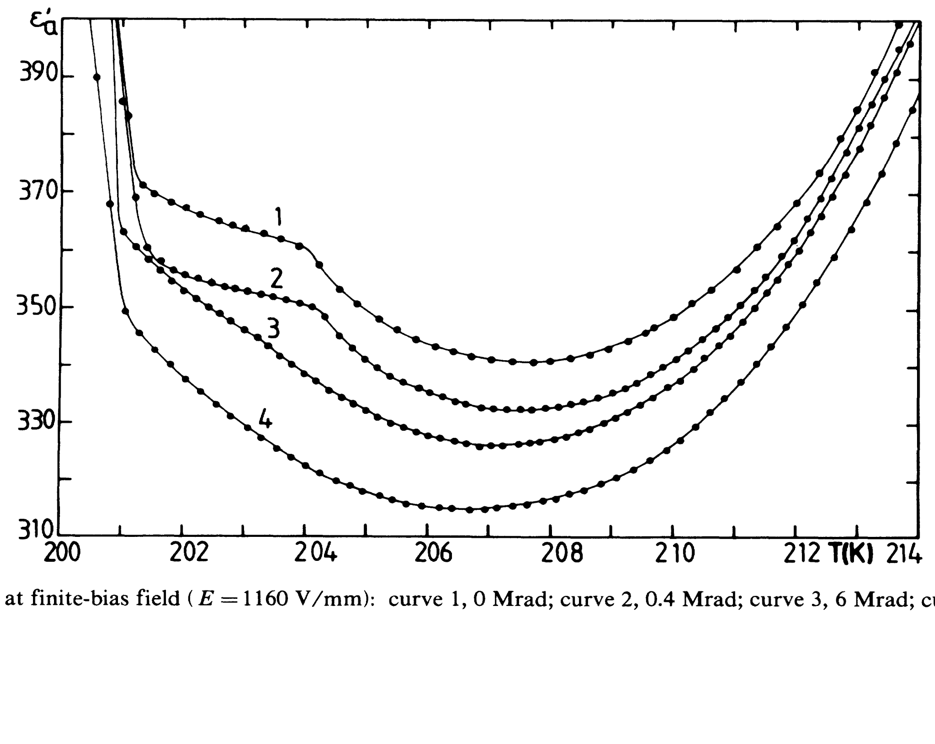

FIG. 5. $\epsilon_a'(T)$ at finite-bias field ($E = 1160$ V/mm): curve 1, 0 Mrad; curve 2, 0.4 Mrad; curve 3, 6 Mrad; curve 4, 90 Mrad.

rapidly with applied field. Eventually, the boundaries of the $\frac{1}{8}$ phase are marked by abrupt changes in the slope of the $\epsilon'_a(T;E\neq 0)$ curve, as illustrated in Fig. 5 (curve 1) for $E=1160$ V/mm.

As a function of radiation dose, the $\epsilon'_a(T)$ curve changes in a qualitative way: The quasiplateau corresponding to the $\frac{1}{8}$ phase is not observed on curve 3 (6 Mrad) and curve 4 (90 Mrad), strongly suggesting that the $\frac{1}{8}$ phase is no longer stable, at least for that value of the applied field. Further comments on this point will be given in Sec. III D.

To summarize the results from dielectric measurements, we remark that we have reached the opposite conclusion from what we set out to prove: Indeed, if the effect of radiation damage is to *destroy* commensurate phases of order 8 or 9, how can x-ray beam exposure *stabilize* commensurate phases of order 15, 29, or 43? In the next sections we hope to show how neutron diffraction measurements on irradiated samples can be used to clarify the above-stated paradox.

III. NEUTRON DIFFRACTION MEASUREMENTS

A. Experimental method

Two specimens of approximate dimensions $10\times 6\times 1$ mm^3 were investigated by neutron scattering. They were cleaved from a large single crystal of the same origin as the plates used in the dielectric measurements (from J. P. Chapelle, Université Paris-Sud, Orsay). Specimen A was first studied in the virgin state, to serve as reference, and was later irradiated at room temperature with a total accumulated dose of 10 Mrad (specimen A'). Specimen B was irradiated under similar conditions, but with a total dose of 100 Mrad.

Neutron measurements were performed on the three-axis spectrometers G4-2 and G4-3, installed on a cold guide at the ORPHEE reactor (Laboratoire Léon Brillouin, Saclay). The spectrometers were operated in the elastic mode, using a Be-filtered incident neutron wavelength of 4.08 Å. Several sets of collimators were used, corresponding to transverse momentum resolutions in the range from 0.0045 Å^{-1} ($0.006b^*$) to 0.0075 Å^{-1} ($0.010b^*$), full width at half maximum.

The position and intensity of the $(2\pm\delta,0)$ satellite reflections were monitored as a function of temperature for specimens A, A', and B. Subsequently, specimen B was used to test the effect of an applied electric field (cf. Sec. III D).

All neutron measurements took place during a 1 to 2 week period after irradiation, a period during which the specimens were kept at room temperature. The annealing rate of irradiation defects at room temperature can be probed by monitoring the time evolution of EPR spectra from irradiated samples:[12] Apart from some short-lived defects, with decay rates of a few hours, most EPR centers appear to be relatively stable, with lifetimes of the order of several weeks. Although it seems natural to assume that nonparamagnetic defects have comparable lifetimes, the values quoted above (10 and 100 Mrad) should be taken as mere indications for the extent of the radiation damage present in the specimens *at the time of the measurements.*

B. Influence of radiation dose on wave-vector hysteresis

Figure 6 shows a comparison between the $\delta(T;E=0)$ curves obtained on sample A and A' (i.e., before and after a 10-Mrad irradiation), while the curve obtained on sample B is shown in Fig. 7. In all three cases, A, A', and B, the same procedure is followed.

(i) The sample temperature is lowered progressively from room temperature to just above T_i.

(ii) Data points are taken at a regular rate of one point per 110 min on cooling. Temperature steps are typically of the order of 1 K (or 0.5 K near a lock-in or potential lock-in transition).

(iii) The same procedure is followed on warming from the ferroelectric phase.

One outstanding feature in Figs. 6 and 7 is the enhancement of the wave-vector hysteresis in irradiated samples. This result is of course expected on the basis of the dielectric data presented in Sec. II above. In the same context, it is interesting to note the different temperature dependence of the dielectric and wave-vector hysteresis as seen in Figs. 2 and 6: While the former vanishes continuously as T_i is approached from below, the latter is only weakly temperature dependent between T_c and T_i. This remark applies equally to the virgin and to the irradiated samples and illustrates the fundamental relationship between the two phenomena. Denoting by Δ the deviations from thermal equilibrium, one readily shows[13]

$$\frac{\Delta\epsilon_a(T)}{\epsilon_a(T)}\propto\eta^2(T)\frac{\Delta q_\delta(T)}{q_\delta(T)}\ , \tag{1}$$

where $\eta(T)$ is the modulation amplitude:

$$\eta^2(T)\propto T_i-T\ .$$

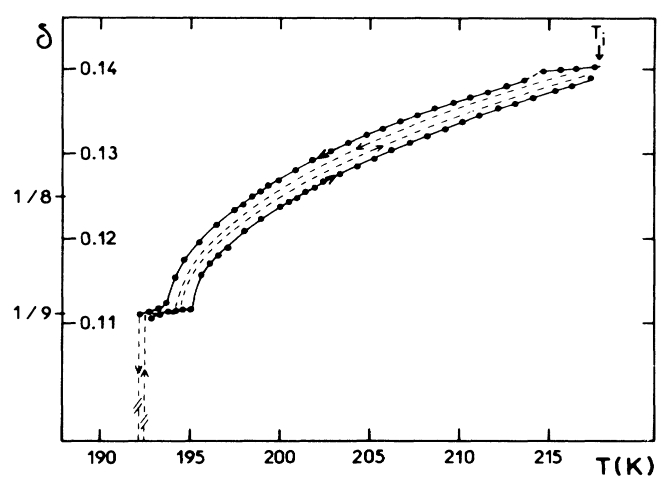

FIG. 6. Modulation wave vector $\delta(T)$ of sample A before irradiation (dashed lines) and after a 10-Mrad x-ray exposure (solid lines).

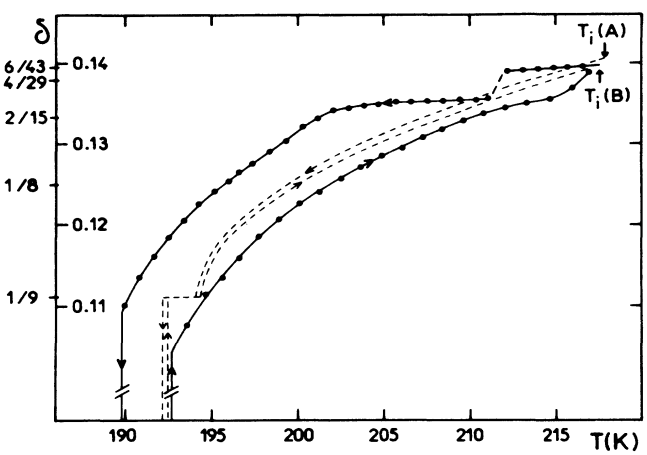

FIG. 7. Modulation wave vector $\delta(T)$ of sample B after a 100-Mrad x-ray exposure (solid lines). The dashed curves are the same as in Fig. 6 (sample A in the virgin state).

C. Commensurate phases and quasiplateaus ($E=0$)

In addition to the enhanced overall hysteresis effect, Fig. 6 shows two anomalous features: (i) a quasiplateau between T_i and T_i-3 K and (ii) an incomplete lock-in at $\delta=\frac{1}{9}$.

Similar but more dramatic effects are visible on the solid curve in Fig. 7: (i) the quasiplateau below T_i now extends over ~ 5 K and is followed by a second, even broader one; (ii) no anomaly is detected, not even a kink in the curve, when $\delta(T)$ passes through the commensurate value $\frac{1}{9}$, on cooling as well as on warming.

The destabilization of the $\frac{1}{9}$ phase in the presence of irradiation defects is also consistent with the dielectric measurements in Sec. II. However, the appearance of quasiplateaus below T_i is a new and unexpected result which, in our view, provides the key to a plausible interpretation of the x-ray results in Ref. 8. We suspect that the extended plateaus observed in the x-ray work had a similar origin as the quasiplateaus seen in Fig. 7, i.e., pinning of the modulation by radiation-induced defects.

We are not able to comment on the difference between ours and the x-ray results. In particular, the plateaus reported in Ref. 8 appeared to be true horizontal steps, corresponding to specific rational numbers:

$$\delta_n=\frac{n+1}{7n+8}\,(n=1,3,5)\ .$$

The steps we observe here are not strictly horizontal, and hence cannot be associated with any particular rational or irrational number. Alternatively, one may look whether, say, the initial value of δ for each plateau is close to a particular rational number.

(i) For the 10-Mrad sample, the plateau begins at T_i with $\delta(T_i)=0.1403\pm2$, which is compatible with $\delta_7=\frac{8}{57}=0.1404$.

(ii) For the 100-Mrad sample, the first plateau also begins at T_i with $\delta(T_i)=0.1397\pm2$ ($\delta_5=\frac{6}{43}=0.1395$), but the second plateau starts at 0.1356 ± 2, which is intermediate between $\delta_1=\frac{2}{15}=0.1333$ and $\delta_2=\frac{3}{22}=0.1363$.

So, the results found in this experiment (i.e., on irradiated samples in zero applied electric field) are reminiscent, but only superficially so, of those obtained in Ref. 8 at large applied fields. In the next paragraph we investigate the effect of this last parameter on the $\delta(T)$ curve from sample B (100 Mrad).

D. Effect of an applied electric field

To be complete, some wave-vector measurements have been performed on sample B (100 Mrad) for two values of the applied field. The thermal procedure is the same as above and the corresponding $\delta(T,E)$ curves are shown in Fig. 8 for $E=0.58$ and 1.16 kV/mm, and for decreasing temperatures. From previous work on virgin samples, one expects to observe a commensurate plateau at $\delta=\frac{1}{8}$ with a temperature width of ~ 3 K for both field values. In fact, no such plateau is observed on the irradiated sample, in agreement with the dielectric data presented above. Instead a wide quasiplateau is observed below $T_i(E)$, followed by a more rapid drop of $\delta(T;E\neq 0)$ with decreasing temperature.

The values of $\delta(T_i,E)$ are 0.1394 ± 2 and 0.1382 ± 2. The first value (for $E=0.58$ kV/mm) is compatible with $\frac{6}{43}$, while the second (for $E=1.16$ kV/mm) is close to $\delta_3=\frac{4}{29}=0.1379$.

The quasiplateaus in Fig. 8 are very comparable to those observed in zero field, in terms of width ΔT and slope dq_δ/dT, and it is likely that the same physical mechanism is at work in both cases. Although the nature of this mechanism is not known in detail (see Sec. III F below), we can state that it is directly linked to the presence of defects in the specimen and not, in any essential way, to the applied field.

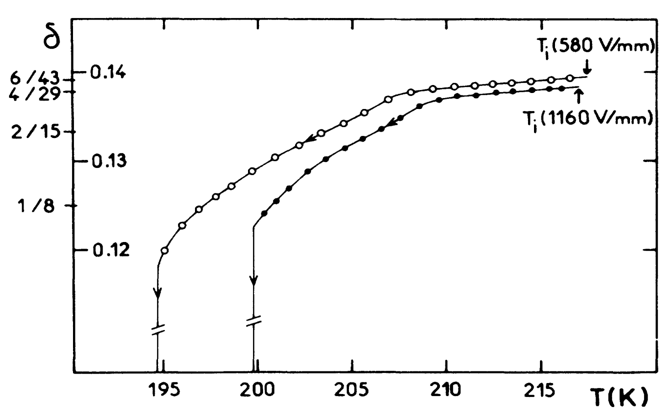

FIG. 8. Modulation wave vector $\delta(T)$ for sample B (100 Mrad) for two values of the applied field (decreasing temperatures only): $E=0.58$ kV/mm (○); $E=1.16$ kV/mm (●).

E. Coherent domain size

It is known on general theoretical[14,15] grounds that frozen impurities, however dilute, break the long-range phase coherence of the modulation in three-dimensional incommensurate systems. However, in most cases the corresponding broadening of the satellite reflections is too small to be detected by conventional diffraction techniques.

Such is the case for high-purity $SC(NH_2)_2$ and $SC(ND_2)_2$, where, even under favorable resolution conditions, satellite and fundamental reflections are found to have the same widths.[7] In heavily irradiated specimens, on the other hand, one may expect the coherence length to become measurable, while simultaneously, the transitions at T_i and T_c should become diffuse.

As pointed out in Sec. II above, no such blurring is apparent in the dielectric response from irradiated samples, and hence it is an open and important question whether a finite coherence length can be detected by satellite-width measurements.

Experimentally, the longitudinal width, $\Delta \mathbf{q}_\delta = \Delta\delta \mathbf{b}^*$, is easier to measure, and, in principle, the relevant instrumental width can be adjusted by using a tightly collimated neutron beam. In order to extract a correlation length from a measured satellite broadening, one must be able to substract the contribution from possible thermal and irradiation *gradients* across the specimen volume.

In the present experiment, the irradiation procedure and the low sample thickness were such that the effect of irradiation gradients, as well as thermal gradients, could be neglected. Under the present experimental conditions, no satellite broadening could be detected as long as the modulation wave vector was "locked" on one of the quasiplateaus shown in Figs. 6, 7, or 8. For sample B a small broadening was observed in the steeper portion of the $\delta(T)$ curves, corresponding to correlation lengths of the order of 100 to 200 unit cells. In contrast to results obtained on other disordered modulated systems,[16–18] no anomalous line shapes (asymmetric profiles or splitting of the modulation into several components) could be detected at any temperature. For the irradiation levels considered here, the concept of a single, well-defined modulation periodicity remains therefore meaningful.

F. Memory effects

Memory effects have been reported[13,19–21] in many modulated systems, such as thiourea, $Ba_2NaNb_5O_{15}$, Rb_2ZnCl_4. Observations are often made on macroscopic properties (e.g., birefringence, dielectric susceptibility), but the microscopic origin of the observed effects is a remarkable *periodicity* memory associated with the presence of *mobile* defects.

The migration of defects in the periodic potential created by the modulation gives rise to what has been termed a "defect density wave" (DDW) (Ref. 13) of same periodicity, and whose amplitude grows with time. Once established, the DDW exerts a pinning potential on the modulation itself, whose effect is to limit the latter's ability to readjust its periodicity in response to a temperature, pressure, or field variation.

Memory effects are observable on nominally-pure systems, but, as in the case of global hysteresis, they become more pronounced with the addition of chemical or irradiation defects. Also, since defect migration is a thermally activated process, the higher the temperature, the shorter the time scale on which memory effects can be detected.

A possible interpretation for the quasiplateau observed below T_i is the formation of a DDW which tends to pin the modulation wave vector at its initial value $\delta_i[\equiv\delta(T_i)]$. The pinning process is not complete, in the sense that, during the time lapse between consecutive measurement points, the "dressed" modulation (i.e., modulation plus DDW) is able to respond to the temperature change, but this response $[\equiv\delta_d(T)]$ is much slower than when the modulation is free from impurities $[\equiv\delta_0(T)]$. Hence the $\delta(T)$ curve measured upon cooling an irradiated sample begins with a quasiplateau corresponding to the dressed modulation response $\delta_d(T)$.

Beyond a certain threshold value for the stored elastic energy $(\propto[\delta_d(T)-\delta_0(T)]^2)$, it becomes energetically favorable for the modulation to break away from the DDW and to revert to its equilibrium periodicity $\delta_0(T)$. This abrupt transition gives rise to the step at the end of the first plateau in Fig. 7. The pinning process can then start again, leading to a second quasiplateau, etc. At lower temperatures, this oscillatory regime is damped out possibly due to pinning by random (fixed) defects which prevent the complete return of the modulation to its equilibrium periodicity.

Evidence for the formation of a DDW is shown in Fig. 7, where the $\delta(T)$ curve measured on *warming* displays a bend at the value of $\delta(T)$ corresponding to the position of the second quasiplateau on the $\delta(T)$ curve observed on *cooling*. In addition, the following experiment was performed on specimen A' (10 Mrad) in order to establish the existence of enhanced memory effects in irradiated samples (cf. Fig. 9).

(i) Starting from room temperature the specimen is cooled and kept at a temperature $T_A=209.3$ K for 19 h. During this "writing" period, no significant relaxation in satellite position, intensity, or width could be noticed.

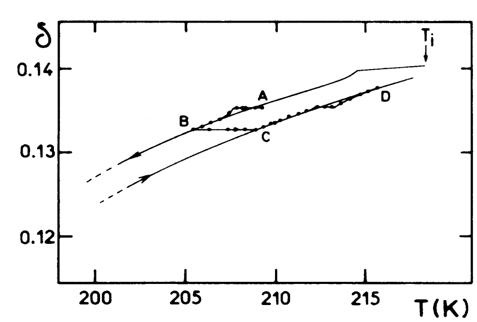

FIG. 9. Direct evidence for periodicity memory in irradiated (10 Mrad) $SC(ND_2)_2$: after a 19-h "writing" period at point A ($\delta_A=0.1353$), a plateau at δ_A is observed on cooling and subsequently on warming.

(ii) Upon cooling at the usual rate (110 min/point), a plateau of ~ 1.6 K is observed.

(iii) At point *B*, the sense of the temperature variation is reversed, and δ remains constant at $\delta_B = 0.1327$ until the warming curve is reached (point *C*).

(iv) $\delta(T)$ follows the warming curve until a value close to δ_A is reached.

(v) A plateau of ~ 1.1 K is observed at $\delta = 0.1354 \simeq \delta_A$.

(vi) After an ~ 2 K crossover region, the normal warming curve is recovered (point *D*).

A similar cycle on the same sample in the virgin state (sample *A*), yielded temperature plateaus narrower by a factor 2, on writing as well as on reading, despite a writing time 4 times longer.

IV. DISCUSSION

From the above experimental results, the effects of x-ray irradiation on the modulated phases of $SC(ND_2)_2$ can be summarized as follows: (a) increase of hysteresis and memory effects; (b) destabilization of commensurate phases ($\delta = \frac{1}{9}, \frac{1}{8}$); (c) appearance of quasiplateaus below T_i in the $\delta(T)$ curve.

The dielectric susceptibility and neutron diffraction data presented above are consistent with results from previous studies on irradiated thiourea specimens.[22,7] In particular, the cooling curve in Fig. 7 is very similar to the data obtained in a previous neutron study (cf. Fig. 4 in Ref. 7). The reason why quasiplateaus were not observed in Ref. 7 is simply that the approximate temperature range ($T > 200$ K) was not explored.

As stated before, the dielectric and neutron results are mutually consistent in so far as points (a) and (b) are concerned. Regarding point (c), we can think of several reasons why quasiplateaus followed by wave-vector discontinuities (as shown in Fig. 7, at $T \simeq 212$ K) may not give rise to dielectric susceptibility anomalies.

(1) One possibility would be that the corresponding anomalies are too weak to be detected: Indeed, the amplitude of the dielectric hysteresis in Fig. 2(b) decreases as $T \rightarrow T_i$, consistent with Eq. (1). At 212 K, it is already quite weak although still within the accuracy of the technique. The wave-vector discontinuity observed in Fig. 7 at 212 K amounts to a sudden variation of more than *a factor 2* in the amplitude of the wave-vector hysteresis. We believe that a comparable discontinuity in the dielectric hysteresis would have been noticed.

(2) More probably, the time scale of the dielectric measurements (6 min/point) is too fast to allow the development of a DDW. An additional experiment with a slower cooling rate is underway in order to clarify this point. It is noteworthy that recent birefringence data[23] on the modulated phase of nominally-pure quartz show a crossover between a smooth regime for fast thermal cycles and a steplike behavior at sufficiently slow speeds (3×10^{-3} K/h).

Finally, we wish to stress that, in our opinion, the above results lend additional support to our original contention that the discrepancy between x-ray and neutron diffraction results arises from radiation damage caused by the x-ray beam. Since then, similar, and even more dramatic effects have been reported[24] in another modulated insulator, $[N(CH_3)_4]_2CoCl_4$, TMATC-Co for short. The authors in Ref. 24 observe continuous changes in the properties of their sample during the course of the experiment: splitting of the modulation into several components with different wave vectors, lowering and smearing of the normal-to-incommensurate transition temperature. They conclude that "x-ray irradiation of TMATC-Co modifies the properties of the incommensurate phase and effectively prohibits a detailed study of the phase transitions in this material."

Our conclusions here will not be as strong, since the doses we have been considering above are easily an order of magnitude larger than in Ref. 24, and the effects we have observed are not as drastic. Of course, it is difficult to compare results from an experiment where the defects are introduced in the modulated state, during the measurement itself, as is the case for Refs. 8 and 24, with the results from an experiment in which the data are taken days or weeks after irradiation. In particular, short-lived defects are not operating in the second case. Therefore, it is not reasonable to expect that x-ray and neutron experiments yield precisely the same $\delta(T)$ curve.

Our purpose in the present study is not to reproduce the results reported in Ref. 8, but to show that x-ray-induced defects do affect the properties of the modulated phases of thiourea, and probably of a host of other materials. Hence great care should be exercised in interpreting x-ray diffraction results from "unknown" modulated compounds. In particular, the common belief that these difficulties are restricted to hydrogen-containing materials awaits wider experimental confirmation.

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