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Effects of defects on the incommensurate phase of sodium nitrite crystals

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Specific-heat measurements on virgin and γ-ray–irradiated single crystals of $NaNO_2$ have been carried out to study the effects of defects on the incommensurate phase. Observation of a small specific-heat anomaly at a temperature just above the commensurate-incommensurate (CI) phase-transition point is reported for the first time. It is suggested that this new anomaly may be evidence for a defect-induced intermediate state between the commensurate and incommensurate phases. We discuss qualitatively the observed new anomaly and thermal hysteresis in the CI phase transition.

I. INTRODUCTION

An anomalous thermal hysteresis has been detected in a number of incommensurate systems, both in insulators and in low-dimensional conductors.[1,2] This hysteresis has been attributed to the effect of pinning of the incommensurate modulation. It is well known from theoretical investigations that the properties of incommensurate systems may be seriously altered by the presence of extrinsic fixed defects or impurities.[3]

In particular, defects (or impurities) and discrete lattice effects become important[4] in the vicinity of the commensurate-incommensurate (CI) phase transition. A metastable chaotic state with randomly-spaced-pinned solitons has been predicted to exist intermediate between the commensurate and incommensurate phases. Furthermore, the randomness caused by the defects as well as the occurrence of competing interactions may lead the systems to have properties similar to those of spin glass.[5]

Thus it is expected that, on the basis of theoretical considerations, changes in the macroscopic properties as well as a limitation on the long-range order of the modulation in incommensurate systems should be observable in the presence of extrinsic defects. Recently, a slow extension of the long-range order of the incommensurate modulation, assigned to the interaction of the modulation with mobile point defects, has been reported.[6]

In this paper, experimental results on the specific heat near the CI phase transition are presented for ferroelectric $NaNO_2$ single crystals which have an antiferroelectric incommensurate phase in the narrow temperature range of 163–165 °C.[7] The incommensurate polarization wave is characterized by the wave vector $\mathbf{q}=\delta\mathbf{a}^*$, where $0.101<\delta<0.122$ with no lock-in at rational fractions like $\frac{1}{9}$.[8] We present the first observation of a small specific-heat anomaly at temperature T_i just above the CI phase-transition point T_c. This new anomaly in the specific heat has sample dependence which may be due to defects in the crystal. To obtain information on the effects of the defects on the incommensurate system, specific-heat measurements were also carried out for γ-ray–irradiated $NaNO_2$ single crystals with various doses. Our measurements support the conclusion that the defects induced by irradiation are responsible for the observed new anomaly and the thermal characteristics in the CI phase transition.

II. EXPERIMENTAL

The specific-heat measurements were undertaken using an ac calorimetry method which is a very effective method for obtaining the detailed temperature dependence of the specific heat near the transition temperature. An ac-modulated light beam (3.4 Hz) serving as a heat source provides periodic heating of the specimen which is mounted in a furnace. The ac temperature of the specimen, which is inversely proportional to the heat capacity of the specimen, was detected through a Chromel-Constantan thermocouple using a lock-in amplifier. The furnace temperature was controlled to provide a slow sweep rate which was normally 500 mK/min and was reduced to about 50–100 mK/min in the vicinity of phase transition.

The single $NaNO_2$ crystals used in this work were grown from melt. For γ-ray irradiation the specimens were exposed to γ rays from a ^{60}Co source (10 kCi) at room temperature. The size of the specimens after polishing is about $2\times2\times0.1$ mm^3.

III. RESULTS AND DISCUSSION

The specific-heat data for the virgin $NaNO_2$ single crystal near its incommensurate antiferroelectric phase are shown in Fig. 1. Since the ac technique does not give absolute values for the specific heat, it was necessary to normalize the experimental data at some temperature. Our data were normalized at $T=195$ °C to the values of the specific heat measured by Sakiyama *et al.*[9] Characteristic anomalies are observed at $T_c \cong 163.5$ °C and $T_N \cong 164.6$ °C which separate commensurate ferroelectric, incommensurate antiferroelectric, and paraelectric phases at these temperatures. Though in both the incommensurate antiferroelectric and the paraelectric phase no difference can be observed, the specific-heat curves show somewhat different behavior from sample to sample near the CI phase-transition point T_c. This fact may be related to the complicated nature of the CI phase transition such as creation and annihilation of domain walls. The phase

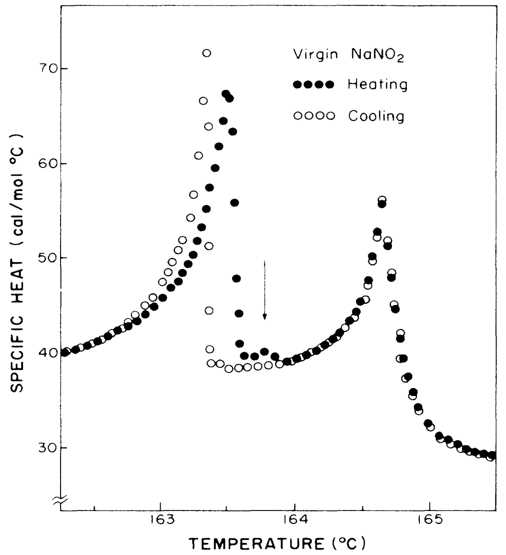

FIG. 1. Specific heat of a virgin $NaNO_2$ single crystal as a function of temperature near the incommensurate phase. The arrow indicates a new anomaly found in this work.

transition at T_c is accompanied by a thermal hysteresis of about 0.2 °C.

A striking feature is the small specific-heat anomaly at temperature $T_i \cong 163.7$ °C just above T_c (Fig. 1). This anomaly was not observed in some samples, and it was detected more clearly during the heating process than during the cooling process. Because of these peculiar aspects it can be inferred that this phenomenon may be due to defects or impurities in the $NaNO_2$ crystal.

The specific-heat data for γ-ray–irradiated $NaNO_2$ crystals are shown in Fig. 2. From these results some interesting features can be noted. (1) The transition temperatures T_c and T_N decrease as the γ-ray dose is increased. The irradiation-dose dependence of T_c and T_N are shown in Fig. 3. Because of their different rates of decrease the temperature range of the incommensurate phase widens as the irradiation dose increases. (2) The thermal hysteresis of the specific heat at T_c becomes conspicuous as the irradiation dose is increased as shown in Fig. 3. This result is in agreement with results for other incommensurate systems in which impurities play a major role in this phenomenon.[10] (3) The small anomaly observed in the virgin crystal becomes manifest for the γ-ray irradiated ones. This anomaly is found in most of the irradiated crystals and is detected more clearly during heating than during cooling as in the case of the virgin $NaNO_2$ crystal.

With regard to the first point, the change in the phase-transition points may be attributed to reduction of electrostatic dipolar interaction due to the point defects induced by irradiation. It is estimated that some sort of short-range interactions as well as the long-range electrostatic interaction are responsible for the appearance of the incommensurate phase of $NaNO_2$.[11] The short-range interactions are likely to be much more influenced by the

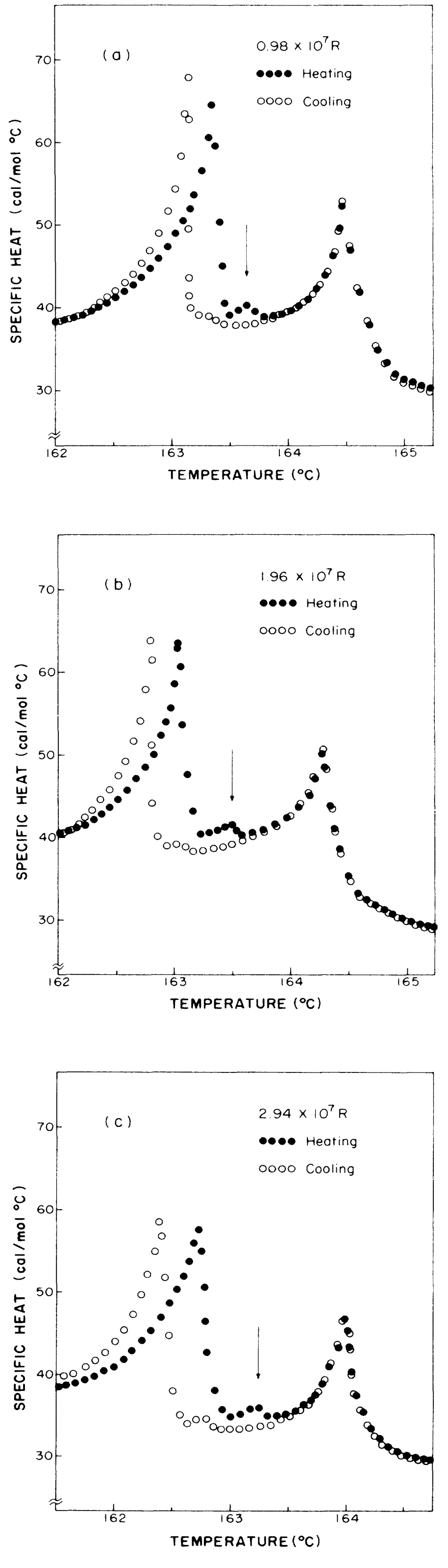

FIG. 2. Specific heat of γ-ray irradiated $NaNO_2$ single crystals as a function of temperature. (a) 0.98×10^7 R, (b) 1.96×10^7 R, (c) 2.94×10^7 R. Arrows indicate a new anomaly found in this work.

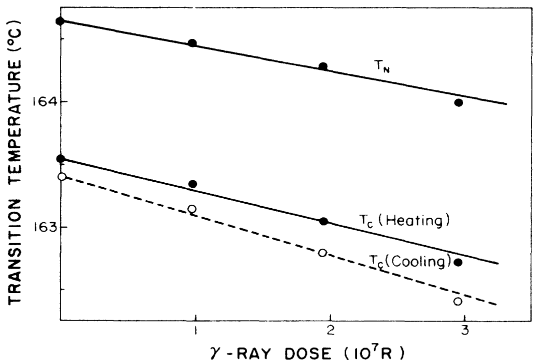

FIG. 3. Transition temperature of virgin and γ-ray irradiated $NaNO_2$ crystals as a function of irradiation dose. The solid and dashed lines are only to aid the eye.

defects, since they are dependent on the overlap of electron clouds between neighboring molecules. Thus it is expected that the long-range order of incommensurate modulation may be destroyed by the defects. The instability of the incommensurate phase seems to be suppressed, with enough disorder to drive the commensurate structure to the incommensurate one, as the defect density increases. Widening of the temperature range of the incommensurate phase can be understood in this way.

For the second point, the enhanced hysteresis phenomenon with irradiation dose can be explained by the pinning of incommensurate modulation by defects. The incommensurate modulation period of $NaNO_2$ must be changed by the processes of creation, annihilation, and diffusion of domain walls when the temperature is varied. These processes are hindered by the defects which tend to pin domain walls in certain favorable locations through the interaction between defects and walls. The attractive interaction between a defect and a domain wall is short range of domain wall width and is exponentially damped at large distances.[3] Thus defect pinning will enhance the hysteresis of a phase transition which requires the motion of domain walls.

Finally let us discuss the new anomaly at T_i in the specific heat of the virgin and γ-ray–irradiated $NaNO_2$ crystals. This anomaly is much smaller than those at T_c and T_N indicating that the entropy change near this anomaly point is very small. Thus a significant change in structure is not expected. This phenomenon is rather considered to be related to defect-pinning effects. This suggestion becomes manifest for the γ-ray irradiated crystals (Fig. 2). Most of the irradiated samples reveal such an anomalous behavior even though some differences are found from sample to sample. It is considered that this may be evidence for a transition from a defect-induced intermediate phase to a regular incommensurate phase. A randomly pinned wall configuration which could be considered as a chaotic state may possibly constitute the defect-induced phase. The transition temperature would be determined by the competition between the wall-wall interaction energy and the defect pinning energy. As the temperature is raised, the defect pinning effects are weakened by thermal fluctuation because the thermal fluctuation can reduce the pinning energy significantly as noted by Rice *et al.*[3] So the randomly pinned domain walls become more regular through the wall-wall interaction, and at some point there is a transition to a regular incommensurate state with creation of domain walls. Different behavior between heating and colling processes can be characterized as a thermal hysteresis caused by defect pinning. A recent numerical study on the stability of chaotic states shows similar features.[12]

X-ray diffraction studies of $NaNO_2$ (Refs. 13, 14) show a small overlap of 0.2 °C between the Bragg and the satellite reflections. Coexistence of domain-wise ferroelectric and incommensurate phases has been attributed to this overlap range.[14] This could be an indication of an intermediate phase between the commensurate and incommensurate phases. It is noteworthy that the temperature range of this overlap is consistent with our measurement of $|T_c - T_i|$ determined from the specific-heat anomalies of virgin $NaNO_2$ crystals. But neutron scattering studies of the modulation wave vector in virgin $NaNO_2$ crystal[8] show that neither a tendency of a lock-in transition towards commensurate or incommensurate state nor a broadening of the satellite reflections is indicated close to T_c. Our specific-heat data of virgin $NaNO_2$ crystal on cooling are in agreement with the neutron scattering studies. The anomalous behavior of the specific heat in a virgin crystal is observed only on heating. This explanation should be tested experimentally by x-ray and neutron diffraction experiments for the γ-ray irradiated $NaNO_2$ crystal. A broadening or destruction of the satellite peaks is expected to be observed in this intermediate phase, especially on heating, and the temperature variation of the satellite peak width should be dependent on the density of defects.

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