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Effect of irradiation-induced defects in the lock-in transition of Rb_2ZnBr_4

M. A. R. Benyacar, E. Cattáneo, H. Ceva, H. Lanza, and L. Schmirgeld
Departamento de Física, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250,
1429 Buenos Aires, Argentina

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We study the changes in the dielectric constant as a function of temperature on Rb_2ZnBr_4 single crystals after irradiation with 22-MeV $^2H^+$ and 108-MeV $^{32}S^{9+}$ ions. Near the commensurate-incommensurate transition our results are interpreted in terms of the nature and amount of defects introduced by the particle irradiation. We observe an anomaly in the dielectric constant in virgin and irradiated samples; we relate it to the temperature dependence of the incommensurate wave vector.

I. INTRODUCTION

Rb_2ZnBr_4 belongs to a family of isomorphous, insulating compounds all displaying an incommensurate (IC) phase before becoming ferroelectric at low temperatures. As is the case for the other members of the group, this phase covers a wide temperature range ($T_c=196$ K, $T_I=346$ K), but it distinguishes itself from the others because the modulation wave vector remains constant over most of this interval, changing only as it approaches T_c.[1,2] This change was interpreted by Iizumi and Gesi[2] as a sample-dependent effect representing the coexistence of regions of different modulation. Experiments made near T_c in this group of materials are usually interpreted by appealing to a phenomenological description whereby the relevant property is the presence of wide commensurate regions, separated by narrow walls (solitons).[3] These walls and regions have been recently observed by transmission electron microscopy in Rb_2ZnCl_4.[4,5] Although the soliton picture is a reasonable frame of reference for IC phases, it turns out that Rb_2ZnBr_4 apparently is never controlled by this regime, judging by the extremely high density of walls, n, present even at T_c ($n \simeq 50\%$).[6] Hence, we believe it is convenient not to use this description here.

Pinning of the modulation wave is at the center of all current interpretations (both continuous and discrete) of the lock-in transition. In any type of crystal there are several contributions to this pinning, such as the discreteness of the crystal lattice, the presence of substitutional and interstitial impurities, and of point and extended defects. This diversity makes it difficult to isolate each contribution in a given crystal. Published works on the effect of defects in this family of incommensurate materials have dealt only with the effect of substitutional impurities [e.g., in Rb_2ZnCl_4 (Refs. 7 and 8)]. Isoelectronic, symmetry nonbreaking (substitutional) impurities are considered in the literature as weak impurities,[9] and are usually described by random changes in the interaction constants[8] ("random bonds").

In this work we report results on the effect of particle-irradiation-induced defects on the dielectric constant of Rb_2ZnBr_4. As irradiation with energetic ions which pass through the sample is expected to produce mainly charged interstitials and vacancies as permanent damage, i.e., strong defects[9] which are described by random-field models,[10,11] we believe this work could shed some light on the contribution of these types of charged defects to the pinning of the modulation wave.

The paper is organized as follows: In Sec. II we give a brief description of the experimental setup; Sec. III deals with our results on the effect of irradiation on the dielectric constant near the lock-in transition. These results make it evident that a relatively small amount of charged defects have a much stronger effect than the isoelectronic ones. Section IV describes an anomaly found in all samples, both virgin and irradiated, between 200 and 215 K. We show that this effect is correlated with the temperature behavior of the modulation wave vector. In Sec. V we summarize our work.

II. EXPERIMENTAL

Crystals of Rb_2ZnBr_4, $a=13.343$ Å, $b=7.656$ Å, $c=9.708$ Å,[12] were grown by very slow evaporation at 300 K from aqueous solutions of rubidium bromide and zinc bromide, which contained an excess of $ZnBr_2$. Large single crystals were grown in plastic vials; b plates of about $5\times5\times0.3$ mm^3 with a minimum of defects (bubbles, inclusions, etc.) were selected in an optical microscope. All hand-polished sections were nearly perpendicular to the b axis with a possible uncertainty of the orientation of a few degrees. Orientation was checked by x-ray diffraction and optical (conoscopic) observation. Neighboring sectors of the same single crystal were used for irradiations involving the same ion beam.

Irradiation was carried out approximately along the b crystal axis in a 10^{-8} Torr vacuum in the 20-MV heavy-ion accelerator TANDAR.[13] During irradiation the temperature of the specimen was kept constant at 40 K in a He closed-circuit cryostat. The beam was adjusted to a diameter of 2 cm and typically currents of 10–15 nA were used.

The dielectric constant along the ferroelectric b axis was measured following the method described by Hamano *et al.*[14] To avoid damage of the samples by the silver paint, chromium electrodes were previously evaporated on the surfaces of the crystals. Dielectric constant measurements were performed in a liquid-nitrogen cryostat, in a He atmosphere. The specimen was cycled at a constant rate of 0.13 K/min. Data were recorded automatically (1000 points each run).

III. DIELECTRIC CONSTANT RESULTS

Measurements of the dielectric constant as a function of T for crystals irradiated with a deuterium ($^2H^+$) beam are shown in Fig. 1. The energy of the beam was 22 MeV and doses of 4×10^{12}, 8×10^{12}, and 3×10^{13} particles, corresponding to irradiation times of 40 min, 80 min, and 5 h (samples 2, 3, and 4, respectively) were used. Deuterium ions are not stopped within the sample (range estimations can be obtained from Ref. 15).

Similar results were obtained by irradiating with $^{32}S^{9+}$, in which case the energy of the beam was 108 MeV and doses of 1×10^{11}, 2×10^{11}, and 4×10^{11} particles, corresponding to irradiation times of 10, 20 and 40 min (samples 5, 6, and 7, respectively), were used. In order to show the details more clearly, only the curve for sample 7 is presented in Fig. 2 with that for the nonirradiated sample. We wish to emphasize that sulphur ions ($^{32}S^{9+}$) are also not stopped within the sample; we checked this by irradiating a pile of two thick specimens, finding that they were both highly irradiated.

General features observed in our experiments on the $\epsilon(T)$ curves follow characteristics previously described in the literature: (i) there is an important asymmetry between cooling and heating runs; on cooling $\epsilon(T)$ does not fall abruptly to its commensurate value but approaches it rather smoothly, while on heating there is a sharp rise of the peak at T_c. (ii) Thermal hysteresis is of the order of 2 K; as far as we know this is the smallest value reported for this compound, showing the overall quality of our crystals.[16] On the high-temperature side of the peak, all curves follow the Curie-Weiss law except for the presence of a conspicuous shoulder in the cooling runs between 215 and 200 K (see Sec. IV).

The influence of irradiation is clearly seen in the changes it produces in the height of the peaks. Although in crystals irradiated with deuterium there is a sizable increase in the full width at half-maximum intensity (FWHMI) of the peaks, this effect is not present in crystals irradiated with sulphur ions. We want to emphasize that the transition temperature (T_c) does not change even after the strongest irradiations, and that no changes are observed in the thermal hysteresis as measured by the difference in temperatures between the peaks in the cooling and heating runs. It should be noted, however, that cooling data for the most irradiated sample show a departure from the general shapes of the curves.

A consistent description of our results can be given as follows: Upon impinging on the samples, the ions have multiple collisions with those of the Rb_2ZnBr_4 crystal, displacing some of them from their lattice sites. We believe Br^- is the more likely candidate to be moved to one of a few interstitial sites available in the structure, leaving a charged vacancy in its place. The effect of irradiation can thus be understood in terms of a random distribution of electric fields, as opposed to the case of substitutional impurities which are generally associated with random interactions. Hence, irradiation-induced defects should have a much stronger effect on the incommensurate modulation wave than substitutional impurities. We be-

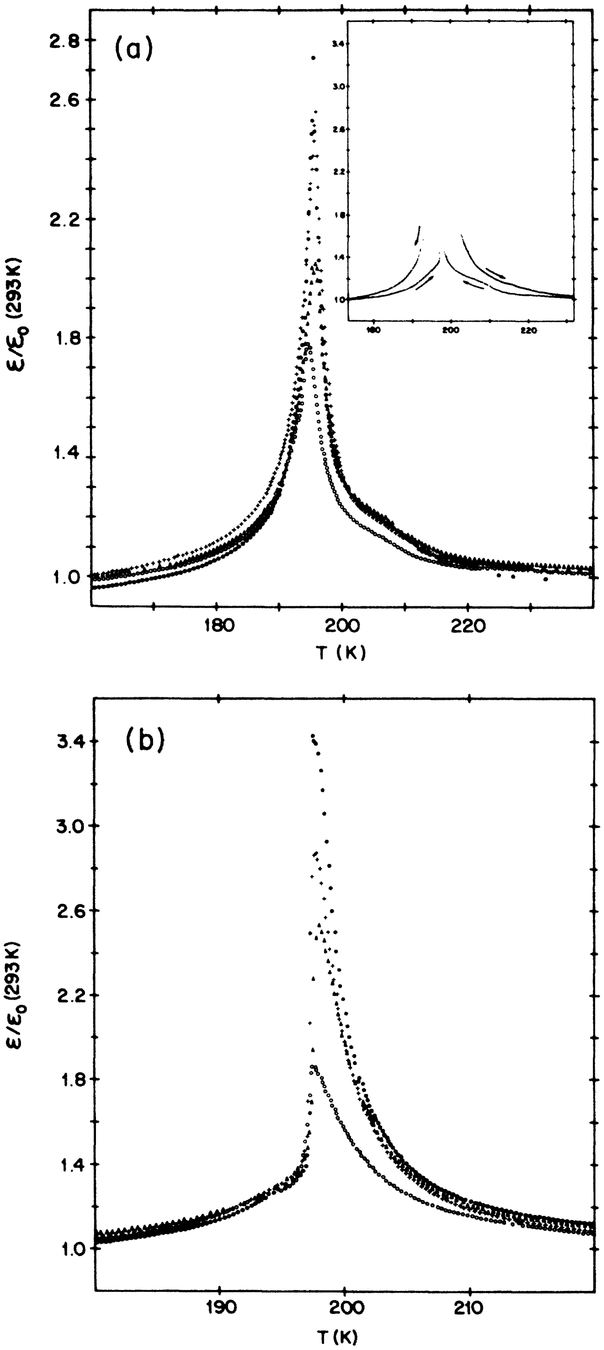

FIG. 1. Dielectric constant ϵ vs T for Rb_2ZnBr_4 irradiated with a 22 MeV $^2H^+$ beam. (a) Cooling runs and (b) heating runs. The closed circle (●) is sample 1, nonirradiated, the plus (+) is sample 2, dose of 4×10^{12} particles, the open triangle (△) is sample 3, dose of 8×10^{12} particles, the open circle (○) is sample 4, dose of 3×10^{13} particles. The inset in (a) shows the thermal hysteresis in the nonirradiated sample.

lieve this difference is central to the interpretation of our results *vis-à-vis* those of substitutional impurities concerning the height of the peak of the dielectric constant. To our knowledge there are no results reported on the influence of substitutional impurities on Rb_2ZnBr_4, but on the isomorphous compound Rb_2ZnCl_4 a reduction of the height of the peak of the dielectric constant by a factor of 3 was obtained by the addition of 1% substitutional K ions.[7] Though it is difficult to estimate the number of displaced atoms, it is reasonable to consider that in experiments in which we obtain a similar reduction, this number is several orders of magnitude smaller than 1%.[17]

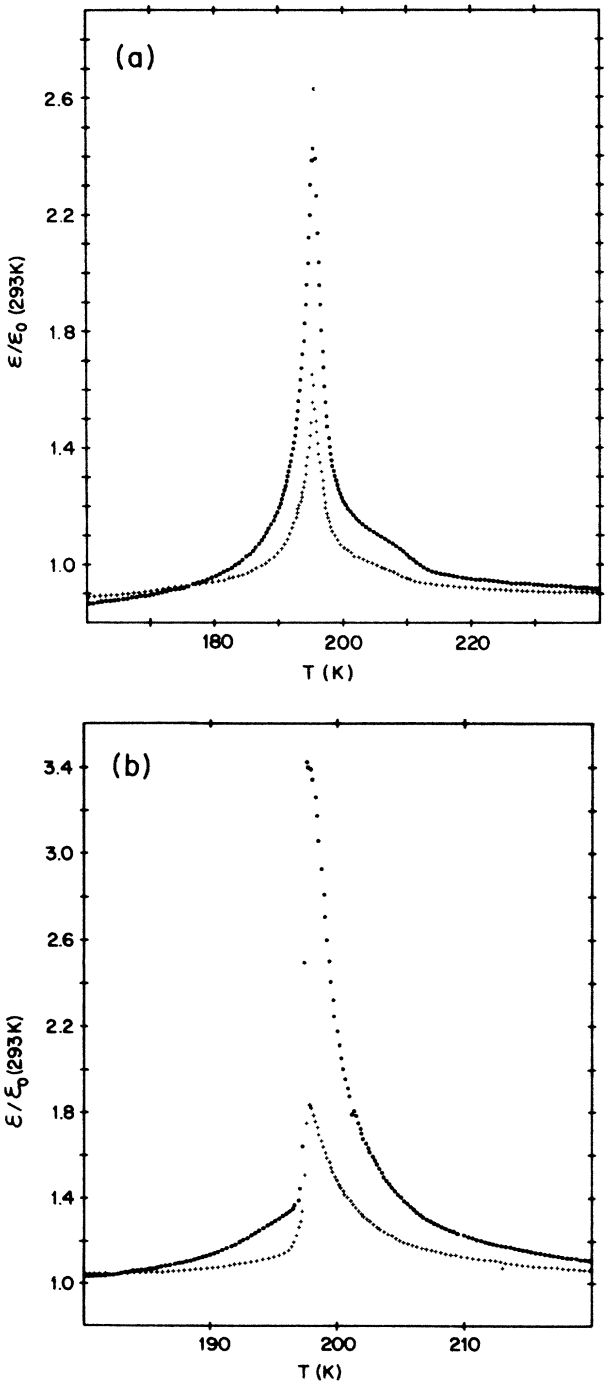

FIG. 2. Dielectric constant ϵ vs T for Rb_2ZnBr_4 irradiated with a 108 MeV $^{32}S^{9+}$ beam. (a) cooling runs and (b) heating runs. The closed circle (●) is sample 1, nonirradiated and the plus (+) is sample 7, dose of 4×10^{11} particles.

The lack of observable changes in the thermal hysteresis[16] in our experiments can be explained by arguments similar to those used to explain the height of the peaks of the dielectric constant. As it follows from our arguments we distinguish between the effect due to the *quality* of the defects, i.e., the presence of displaced charges, and that due to the *amount* N of these defects present. If the mean random electric field averages to zero we do not expect, from the electrical point of view, a modification in T_c. The only remaining factor is then related to N and is too small to be observable.

The increase of the width of the peaks measures the disorder present in the samples as illustrated in the behavior of samples 4, 3, and 7 which have been irradiated with a number of particles in a proportion of 80:20:1 showing an increase in the FWHMI with respect to the nonirradiated one of 100%, 50%, and 0%, respectively. Although it is obvious that each $^{32}S^{9+}$ ion more strongly distorts the lattice than the $^{2}H^{+}$ ions, in what concerns the width of the peaks this effect is overcome by that due to the number of incident particles.

IV. DIELECTRIC CONSTANT ANOMALY

An interesting by-product of our results is an anomaly in the dielectric constant which can be observed only in the cooling runs, between 215 and 199 K, which we have found in all samples, including the virgin ones. Moreover, only the strongest irradiations have any effect on it (see Figs. 1 and 2). To isolate this effect we have substracted a temperature-independent contribution

$$\epsilon''(T)=\epsilon(T)-\epsilon(293\text{ K})\ ;$$

a Curie-Weiss law adjusted to the rising part of the main peak was then substracted from $\epsilon''(T)$. In this way we found a broad ($\Delta T \simeq 15$ K) peak with a height approximately equal to 4% of that of the main one (Fig. 3). Due to the smallness of this effect only very careful and de-

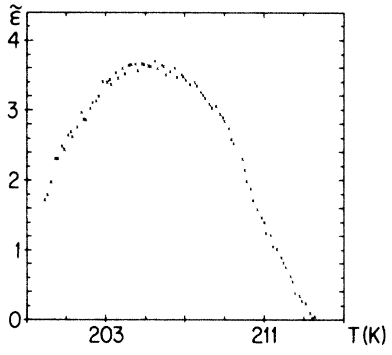

FIG. 3. Anomaly in the dielectric constant between 199 and 215 K, observed in cooling runs. The procedure for isolating this peak is described in the text. The height of the peak is approximately 3–4 % of that of the main one.

tailed measurements of the dielectric constant can show it up.

In the same range of temperature the modulation wave vector **q** ceases to be constant,[1] and Iizumi and Gesi[2] have shown the presence of sample-dependent multiple satellite diffraction peaks.

V. SUMMARY

In conclusion, and assuming that the main permanent defects introduced are charged interstitials and vacancies, we have consistently interpreted our data on changes in the height of the peak of the dielectric constant and on the lack of changes in the hysteresis. These experiments show that strong defects introduced by irradiation with energetic ions have a much bigger effect than substitutional impurities in agreement with theoretical ideas which describe both situations by means of random fields and random bonds, respectively. Work on a phenomenological model which could explain the influence of these defects on the height of the peaks is in progress.

Additionally we have found a (small) peak in the dielectric constant at the temperature where the modulation vector ceases to be constant. This phenomenon is not related to irradiation-induced defects. Similar measurements which are currently being performed on Rb_2ZnCl_4, in which the modulation vector changes continuously with temperature, do not show this anomaly giving support to this interpretation.

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[16] It is well known that thermal hysteresis is mainly controlled by the quality of the crystals. What we would like to stress from our experience with this material, is that this means not only having a small amount of impurities but also of other defects such as bubbles, observable at an optical microscope scale even in apparently nice transparent crystals. In effect, we have obtained thermal hysteresis as large as 4 K in samples coming from the same batch as reported here, i.e., with the same amount of impurities, but containing bubbles and/or inclusions. All measurements reported in this paper were performed on samples selected from nearby bubbleless sections from the same single crystal. In this context we have found that crystals of Rb_2ZnBr_4 grown by us with 1% potassium are less perfect than those nominally pure, making it difficult to isolate in them the effect of impurities from those due to other types of crystalline defects.

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