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NOVEL INCOMMENSURATE PHASE IN $Cs_3Bi_2I_9$

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The incommensurate modulation has been found in the hexagonal $Cs_3Bi_2I_9$, belonging to the $A_3B_2X_9$ family of the layered compounds. The second order normal-incommensurate transition at $T_i = 224$ K is accompanied by the symmetry change $P6_3/mmc \leftrightarrow P2_1/m$. The transition into a ferroelastic incommensurate phase occurs at the zone center, according to the NQR and ultrasonic measurements. © 1998 Elsevier Science Ltd

1. INTRODUCTION

The $Cs_3Bi_2I_9$, belongs to a very vast family of the layered $A_3B_2X_9$ compounds, where A = alkaline metal; B = Fe, As, Sb, Bi, Tl, Cr, W, Mo; X = Cl, Br, I [1, 2]. The CsI_3 hexagonal layers form the close-packed stacking where every Cs atom has twelve I-atoms as nearest neighbours. The $Cs_3Bi_2I_9$ has the hcc-stacking sequence and $P6_3/mmc$ space group at room temperature. The Bi-atoms occupy octahedral interstices where they are surrounded by six I-atoms, only two-thirds of octahedra are filled by Bi-atoms. In the structure of hexagonal $Cs_3Bi_2I_9$ octahedra are jointed by face forming bi-octahedral $[Bi_2I_9]^{3-}$-ions.

The different types of $A_3B_2X_9$ structures are widely investigated at room temperatures, however the knowledge on phase transitions was very restricted [1, 3]. Very recently interesting low temperature phase transitions have been found in two representatives of $A_3B_2X_9$ family: $Cs_3Bi_2I_9$ [4] and $Cs_3Sb_2I_9$ [5]. Phase transition in $Cs_3Bi_2I_9$ have been studied using X-ray and nuclear quadrupole resonance (NQR) frequency measurements on powder samples. In the present paper detailed measurements of ^{127}I NQR line shape below transition point have been performed on single crystal samples to determine the type of lattice instability. The measurements have revealed the unusual phase transition into ferroelastic incommensurate phase.

2. EXPERIMENTAL

The crystals of $Cs_3Bi_2I_9$ have been grown by Bridgemen method.

The ^{127}I NQR spectra have been obtained with spin-echo spectrometer in the temperature interval 86–300 K and at 77 K. At room temperature two NQR lines were found at the frequencies 100.11 and 120.29 MHz.

In $Cs_3Bi_2I_9$ the temperature dependences of the NQR frequencies reveal a second-order phase transition at the temperature $T_i = 224 \pm 1$ K (Fig. 1). Below the transition point the NQR lines have the anomalous shape of continuous frequency distribution limited by edge peaks (Fig. 2). This type of inhomogeneously broadened NQR-lines occurs when three-dimensional periodic structure is modulated along one crystallographic direction by long-periodic wave and the ratio of the two periods is an irrational number, i.e. an incommensurate structure arises below T_i [6]. Figure 2(a) shows the line shape evolution below the normal-incommensurate transition temperature. One can see the appearance of the third singularity near 216 K in the center of the frequency continuum. The intensity of both edge and central peaks gradually increases with temperature lowering at the cost of the continuum. The residual continuum between the edge peaks disappears under the spectral noise at nearly 205 K for the ν_2-component and at ~200 K for the ν_1. The gradual redistribution of the intensity between the lines is going down to ~160 K with the temperature decrease. At low temperatures complete NQR spectrum consists of five singlet lines with nearly equal intensities down to liquid nitrogen temperature limiting our measurements. The bi-octahedral $[Bi_2I_9]^{3-}$ ion has three "bridge" iodines belonging to the common face and six "terminal" iodines [1, 2]. In the hexagonal phase these two kinds of I-ions are chemically (structurally) non-equivalent, however I-ions of one kind are equivalent. The symmetry lowering at the transition is $P6_3/mmc \leftrightarrow P2_1/m$ [4]. Accordingly there appear three

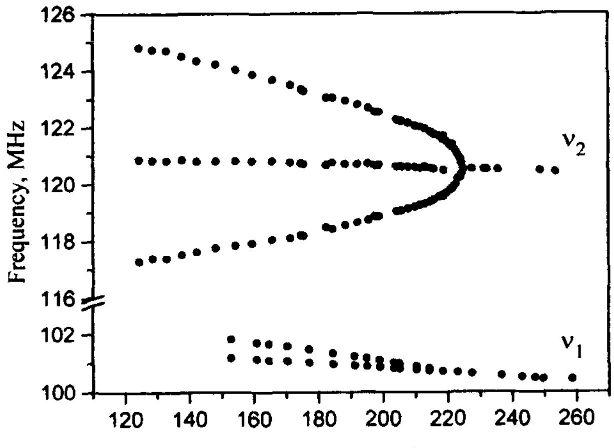

Fig. 1. The temperature dependences of the ^{127}I NQR frequencies of the spectral peaks. ν_1-"bridge" iodines; ν_2-"terminal" iodines.

"terminal" and two "bridge" structurally non-equivalent iodines, which is reflected in the number of the NQR lines at low temperature: three higher frequency lines come from three "terminal" iodines, while two others, i.e. low-frequency lines originate from the "bridge" iodines.

In most cases an incommensurate structure exists in a certain temperature interval between a normal–incommensurate (T_i) transition and an incommensurate–commensurate "lock-in" transition point (T_L) where the structure restores a three-dimensional translational periodicity. In $Cs_3Bi_2I_9$ the change of the line shape below T_i follows in outline the scenario of the incommensurate modulation evolution from the "plane wave limit" near T_i to the "multisoliton limit" just above T_L [6]. Theoretically the intensity of the frequency continuum falls to zero at T_L, because below T_L structure becomes commensurate again. Simultaneously the intensity of the spectral peaks which corresponds to the quasi-commensurate domains above T_L increases noticeable. Experimentally a lock-in transition point usually is well-observed as the rapid increase (or jump) of the peak intensities. The frequency continuum disappears under the spectral noise somewhat above T_L, depending on the signal-to-noise ratio. Thus below the level of the spectral noise the information on the intensity of the residual frequency continuum is lost. The type of the NQR spectra of the $Cs_3Bi_2I_9$ near 205 K shows that the quasi-commensurate domains are formed already and the soliton density is relatively low. Nevertheless the peak intensities change monotonously into the broad temperature region so that it is impossible to define the transition temperature T_L from the NQR data.

One should mention the unexpectedly strong influence of the mechanical treatment of the samples on the NQR line shape in the incommensurate phase. The

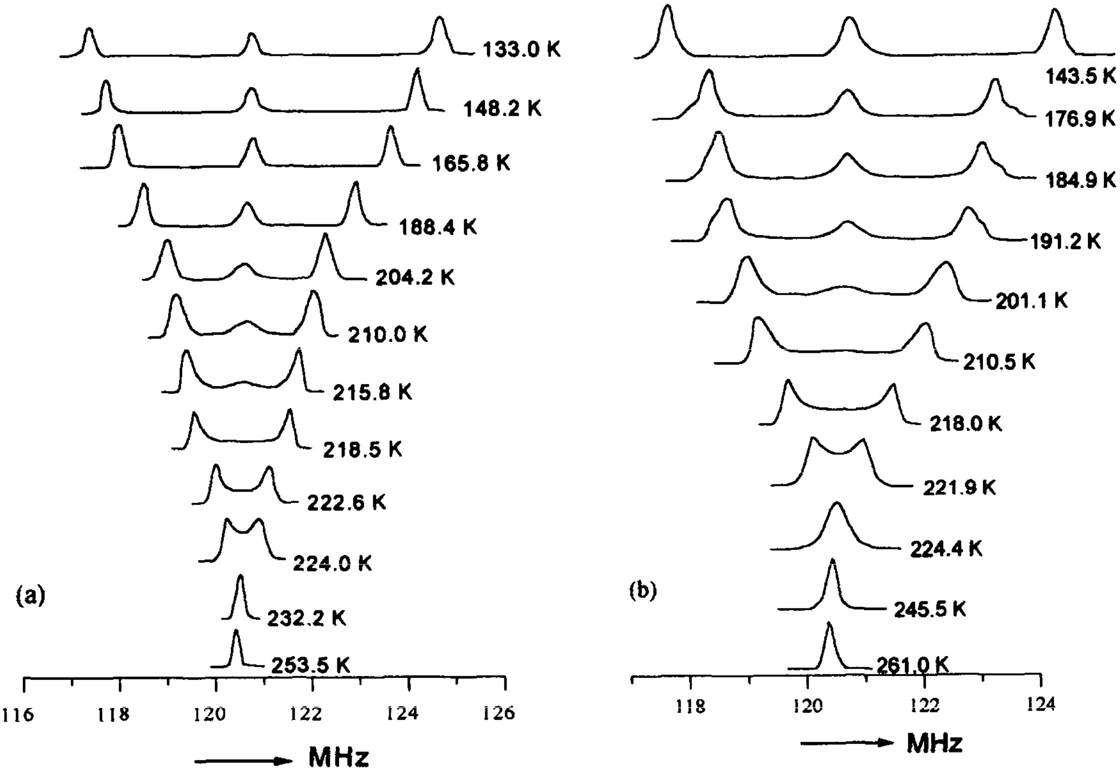

Fig. 2. The line shape of the ν_2-component at the different temperatures. a – single crystal sample; b – powder sample

spectra obtained from the samples made by grinding of the large single crystals show the shape of frequency continuum [Fig. 2(b)] somewhat different from one obtained from single crystals. At low temperatures the frequency continuum on Fig. 2(b) is overlapped with another continuum (or continuums) with growing splitting between singularities. This continuum first is seen as a shoulder-structure of the "main" continuum. The intensity between edge peaks is noticeably higher than in the case of single crystal sample and the residual incommensurate continuum is observed down to nearly 143 K. Below this temperature the NQR spectrum consists of singlet lines only. The relative intensity of the additional continuum changes from sample to sample. The long annealing (~4 h) at high temperature (~530 K) diminishes the difference between the spectra of powder samples in the incommensurate phase. Simultaneously the line shape becomes more close to one observed in the single crystal at the corresponding temperature. These data show that the influence of external strains on modulation in $Cs_3Bi_2I_9$ could be interesting as the special topic.

The temperature dependences of the elastic stiffness have been measured along the main axis by the pulse ultrasonic method at 10 MHz in the hexagonal phase. The velocity of shear wave along [0 0 1] is about 5×10^4 cm s^{-1} at room temperature. The C_{44} elastic constant is strongly temperature dependent as it is shown on Fig. 3. The ultrasonic attenuation at the approaching of the transition point T_i prevents the measurements below 237 K, where the velocity diminishes to 2.5×10^4 cm s^{-1}.

3. DISCUSSION

The NQR data presented above show the existence of the structural incommensurability in the family of the layered structures $A_3B_2X_9$. Extensive studies should be performed to get sufficient information on the character of incommensurate phases in these crystals. Some essential comments however can be made at present.

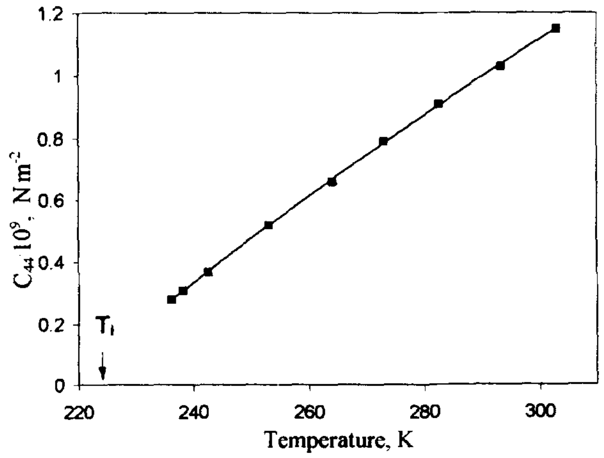

Fig. 3. The temperature dependence of the C_{44} elastic constant along main axis.

Both the change of the number of the NQR lines in $Cs_3Bi_2I_9$ with temperature lowering and the temperature behaviour of the C_{44} elastic constant near T_i show that the transition occurs at the center of the Brillouin zone.

The incommensurability appearing near $q = 0$ is the case when the Lifshitz invariant does not exist. However Levanjuk and Sannikov have shown that the interaction of the order parameter with another variable can lead to the appearance of the incommensurate structure if so-called invariant of the Lifshitz type is allowed by symmetry [7]. In our case such an invariant can come from the interaction between spatial derivatives of the order parameter (η) and strain tensor component U_{ij}. Such a case occurs in quartz, which has a hexagonal symmetry in a normal phase and incommensurate modulation arising near $q = 0$ [8].

The group-theory analysis for the transition with symmetry lowering from $P6_3/mmc$ to $P2_1/m$ was made in [9, 10]. The active representation changing the symmetry is the two-dimensional representation E_{1g}. Only one of two components generates the $P2/m$ monoclinic structure. At $q = 0$ this component couples with the acoustic branch with $q = (0, 0, q_3)$ that corresponds to double-degenerated E_{1u} representation. One of the E_{1u} components induces the shear strain S_5 which should lead to softening of the C_{44} elastic constant near T_i, exactly as it is observed in $Cs_3Bi_2I_9$. Possibly the model developed in [7, 8] may be taken as a guide-line to explain the origin of the incommensurate phase in $Cs_3Bi_2I_9$.

The other special feature of $Cs_3Bi_2I_9$ is that a monoclinic structure appears just below T_i, as shown in the X-ray powder patterns [4]. In most known cases the star of q_0 has 2 branches ($-q$ and q) and the averaged structure of the incommensurate phase has the same space group as that of the normal phase. However if the normal phase is of the $P6_3/mmc$ symmetry and the star of q_0 has six branches, then the symmetries of the normal and incommensurate phases can be different [11]. Modulation in such a case may be multidimensional. The shape of the anomalous NQR line in the incommensurate phase depends on the dimensionality of the modulation. However the deviation from the one-dimensional case is determined by the ratio of the modulation amplitudes existing along different directions. It may be imperceptible if the difference in the amplitudes is less than half of the order of the magnitude and the width of the individual spectral component of the frequency continuum is relatively large. Our preliminary X-ray single crystal measurements show patterns which are very complicated below T_i involving both a specific six-twin structure and a small value of the "incommensurate" misfit δ. An attempt to determine quantitative characteristics of the modulation will be performed by high-resolution neutron diffraction.

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