Phase transitions in the $(Cs_{1-x}Rb_x)_2ZnI_4$ system

A. A. Sukhovskiĭ, V. V. Lisin, I. P. Aleksandrova, and V. N. Voronov

A. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

J. J. Melero

Saragossa University, 50009 Saragossa, Spain
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$(Cs_{1-x}Rb_x)_2ZnI_4$ crystals were grown by two different methods with Rb concentrations varying from $x=0$ to 2.5%. ^{127}I NQR and calorimetric measurements showed that crystals grown by the Bridgman technique contain residual impurities ($\sim 0.5\%$) for all x. While $x=0$ crystals grown from solution do not contain detectable impurities, they allow incorporation only of a low Rb concentration, not above 0.5%. A transition-temperature–concentration (x) phase diagram has been constructed for Bridgman-grown crystals from NQR data. Rb doping shifts the normal-incommensurate and incommensurate-ferroelastic phase-transition points toward higher temperatures with different rates. The $P2_1/m \leftrightarrow P1$ first-order transition shifts toward lower temperatures. The region of low Rb concentrations lies closest to the critical point.
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Studies of defect interaction with incommensurate (IC) structure belong to an independent and well-developed area in the physics of aperiodic systems. While this subject includes several phenomena occurring only in IC modulated crystals, each such investigation starts from the assumption that the phase diagram of the system within a certain interval of impurity concentrations x is known.

We are reporting a ^{127}I NQR and calorimetric study of the $(Cs_{1-x}Rb_x)_2ZnI_4$ system within the Rb concentration region $x=0-0.025$. There are several publications on the phase transitions in undoped Cs_2ZnI_4 (Refs. 1–6) and symmetry measurements in the phase transition sequence[2]

$$Pnma\ (Z=4) \leftrightarrow IC \leftrightarrow P2_1/m\ (Z=8) \leftrightarrow P1\ (Z=4).$$

The phase-transition temperatures of crystals grown from solution, as determined under cooling, are $T_i=120.5$ K for the normal-IC phase transition, $T_{c1}=108$ K for the lock-in transition, and $T_{c2}=96$ K for the low-temperature first-order transition.

Interestingly, the coefficient ratio $\beta_2/\beta_1=0.44$ (Ref. 3) of the thermodynamic potential describing the phase transition sequence in the theoretical model of Cs_2ZnI_4 is characteristic of the so-called strong-anisotropy case, where the system is close to the Lifshits-type critical point[7]. Doping a crystal is one of the ways to bring the system to a singular point on the phase diagram and to study it. Unfortunately, predicting the direction of doping-induced displacement of a system in complex structures is virtually impossible; it is established experimentally and is one of the goals pursued in phase diagram studies.

1. EXPERIMENT

A. Crystal growing

Crystals of undoped Cs_2ZnI_4 were grown previously from water solution. This method was employed also to grow doped crystals, but we did not succeed in increasing the Rb concentration in solution-grown crystals above $x=0.005$. The Bridgman method was employed to prepare crystals with higher Rb concentrations. The crystals were grown in quartz ampoules in an argon ambient. The starting reagents were purified by repeated recrystallization. Crystals with Rb content $x=0$, 0.0011, 0.005, 0.01, and 0.025 were obtained. The rubidium content for small concentrations (up to $x=0.005$) was determined by plasma absorption analysis, and for high x, by x-ray fluorescence. It was established that the Rb concentrations in grown boules coincide within experimental error with those in the starting charge.

B. NQR

For conveniency in comparison, Fig. 1 reproduces the data of Ref. 2 obtained for an undoped Cs_2ZnI_4 crystal grown from water solution. The temperature dependences of the NQR frequencies at the lock-in transition (T_{c1}) exhibit breaks which permit determination of the transition point T_{c1} to within ~ 0.5 K. The normal-IC phase-transition point (T_i) is determined to within 1–2 K because of a partial overlap of the lines belonging to the normal and IC phases, which is associated with the presence of transition precursor clusters above T_i.

Figure 2 presents temperature dependences of the ^{127}I NQR frequencies for a solution-grown crystal with Rb concentration $x=0.0018$. Even such a low concentration of the Rb impurity affects strongly the shape of the ^{127}I NQR spec-

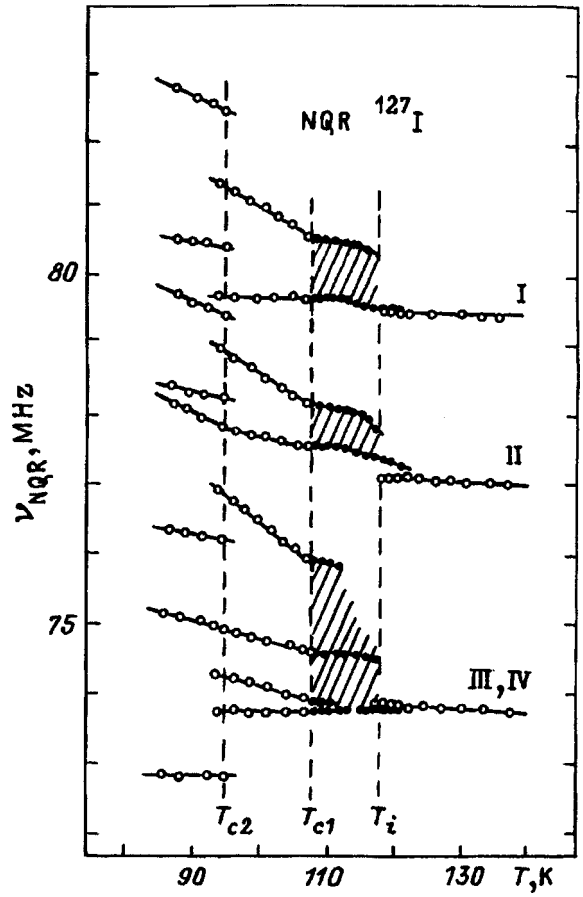

FIG. 1. Temperature dependence of NQR frequencies in solution-grown Cs_2ZnI_4 (from data of Ref. 1).

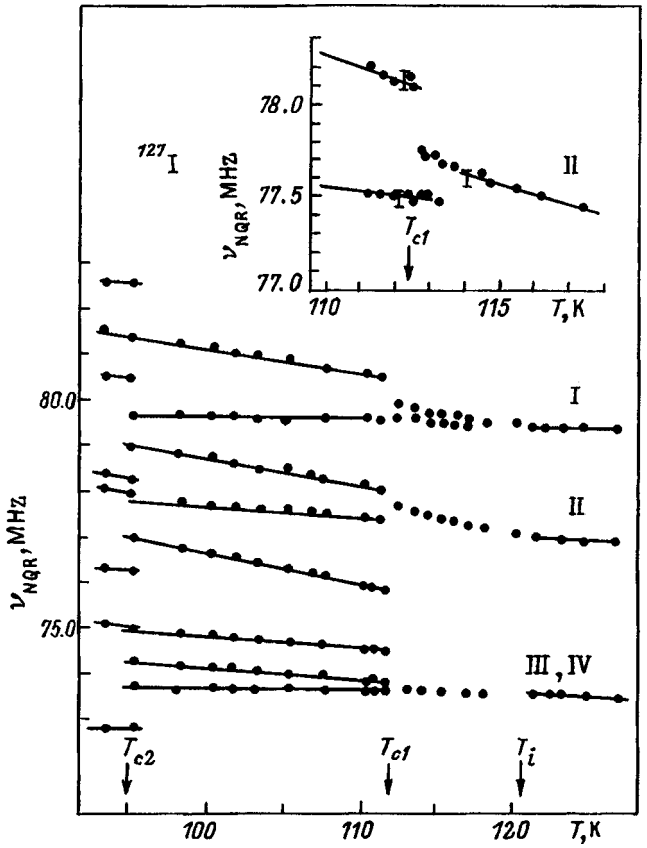

FIG. 2. Temperature dependence of NQR frequencies in solution-grown $(Cs_{1-x}Rb_x)_2ZnI_4$ ($x=0.0018$). Inset: region near T_{c1} for the spectrum component II.

trum in the IC phase compared to the undoped Cs_2ZnI_4. The undoped crystal exhibits an anomalous line shape characteristic of one-dimensional modulation, namely, a continuum frequency distribution bounded on both sides by peaks. A characteristic feature of Cs_2ZnI_4 is that, just below T_i, one of the side singularities is suppressed and is barely seen against the background. This singularity grows, however, in intensity with decreasing temperature, so that at approximately 5 K below T_i the spectrum takes on the shape typical of the IC phase.[2] In the doped crystal, the second singularity remains suppressed throughout the temperature region of existence of the IC phase. The only feature left in the spectrum from the IC continuum is one asymmetrical side singularity. Above T_i, the clusters, transition precursors, disappear in doped crystals. However in this case one also cannot determine the transition temperature to better than 1 K, because there is an interval near the transition where the line becomes washed out by noise as a result of the specific behavior of nuclear quadrupole relaxation.

The lines of the third phase become discernible against the background below T_i, with their intensity reaching a maximum within ~ 0.5 K. A region has been found where the residual peaks of the IC phase and the C-phase lines coexist (~ 0.5 K, see inset in Fig. 2). While the transition at T_{c1} appears more clearly pronounced first order than that in the undoped crystal, this observation should be checked in studies of the temperature dependences of the wave vector q_δ, which yield a more complete information on the character of a lock-in transition. The transition temperatures for the solution-grown, doped ($x=0.0018$) crystal are, within experimental errors, $T_i=121.0\pm 1$ K, $T_{c1}=112.0\pm 0.5$ K, and $T_{c2}=95.0\pm 0.5$ K.

The temperature dependences of NQR frequencies for Bridgman-grown crystals with Rb concentrations $x=0$, 0.001, 0.005, 0.01, and 0.025 were obtained in the region from 170 to 110 K. Figures 3 and 4 present the temperature dependences of the frequency for the spectrum component II for the lowest, $x=0$, and maximum, $x=0.025$, Rb concentrations. Similar dependences obtained for the intermediate concentration region follow the behavior shown in Figs. 3 and 4, if one takes into account the shift of the transition points along the temperature scale with Rb concentration.

Note that the spectrum of the undoped crystal grown by the Bridgman technique resembles not that of the ''pure,'' solution-grown Cs_2ZnI_4 but rather the spectrum of the crystal with a low Rb concentration ($x=0.0018$). The phase-transition point T_{c1} is shifted toward higher temperatures to become 112.0 ± 0.5 K. While the shift in T_i is just at the experimental accuracy limit, it nevertheless is seen clearly (121.6 K). A comparison of crystals with close Rb concentrations, $x=0.0018$ and $x=0.0011$, grown by the two different methods shows that the transition points T_i and T_{c1} in the Bridgman-pulled crystal are shifted noticeably toward higher

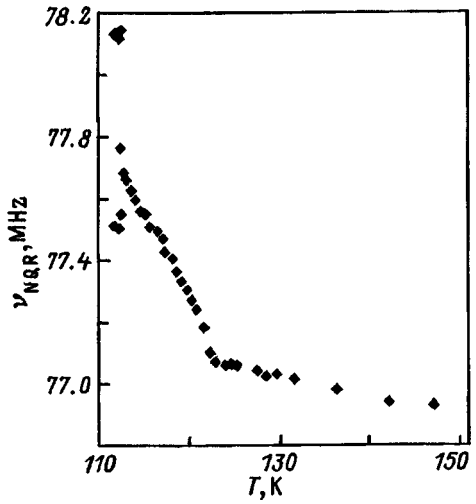

FIG. 3. Temperature dependence of NQR frequencies in Bridgman-grown Cs_2ZnI_4 ($x=0$).

temperatures. The dependence of the first-order transition temperature T_{c2} on x was derived from the jump in frequency of component I at the transition. The Rb concentration $\sim 2.5\%$ is the upper limit for NQR studies of the $(Cs_{1-x}Rb_x)_2ZnI_4$ system. In addition to the NQR lines of this crystal being broadened substantially already in the initial phase, weak broad lines not characteristic of the rhombic phase of Cs_2ZnI_4 appear in the spectrum.

The transition temperatures obtained for the above-mentioned Rb concentrations from the temperature dependences of the NQR frequencies are given in Table I.

C. Calorimetric data

Calorimetric data were obtained for solution-grown crystals with the minimum concentration $x=0.0018$ (Fig. 5). The measurements were performed on a SinkuACC-1VL calorimeter within the 80–300 K temperature region. The

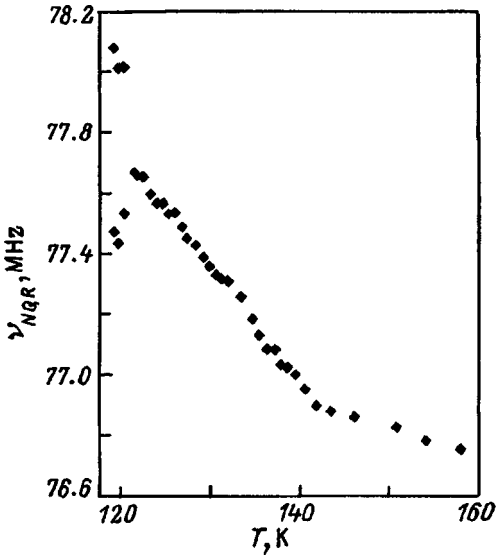

FIG. 4. Temperature dependence of NQR frequencies in solution-grown $(Cs_{1-x}Rb_x)_2ZnI_4$ ($x=0.025$).

TABLE I. Phase-transition temperatures for $(Cs_{1-x}Rb_x)_2ZnI_4$ derived from the temperature dependences of NQR frequencies.

Growth method	Rb concentration, x	T_i, K	T_{c1}, K	T_{c2}, K
Melt	0.0	120.0±1.0	108.0±0.5	96.0±0.5
Melt	0.0	121.6±1.0	112.7±0.5	96.3±0.5
Melt	0.0018	121.0±1.0	112.0±0.5	95.0±0.5
Melt	0.0011	124.5±1.0	115.0±0.5	95.3±0.5
Melt	0.005	127.6±1.0	115.0±0.5	92.4±0.5
Melt	0.01	131.2±1.0	117.5±0.5	90.3±0.5
Melt	0.025	142.0±1.0	120.6±0.5	?(<78 K)

samples were 0.1-mm thick plates coated by black carbon paste to improve heat absorption. The conditions of heat capacity recording are similar to those described in Ref. 3. For $x=0.0018$, the anomaly corresponding to the transition at T_i is observed at the same (within experimental error) temperature of 117.0 ± 0.08 K as in the undoped, solution-grown crystal[3]. The anomaly is slightly washed out compared to the data quoted in Ref. 3, which is seen from the decrease by a few percent of the height of the step in the heat capacity curve corresponding to T_i. The anomaly at T_{c1} (the lock-in transition) is washed out strongly and is substantially lower, but its peak is observed to lie at the same temperature as in pure Cs_2ZnI_4. The first-order transition $P2_1/m \leftrightarrow P_1$ at T_{c2} is shifted down by 0.4 K, and the heat capacity anomaly decreased somewhat in height.

2. DISCUSSION OF RESULTS

Figure 6 presents the phase diagram constructed from NQR data for Bridgman-grown crystals in the transition-temperature–concentration x coordinates. As x increases, the phase-transition points T_i and T_{c1} shift toward higher temperatures, and T_{c2} moves rapidly to lower temperatures.

The region of existence of the IC phase in the phase diagram expands somewhat with increasing impurity concentration. Because the IC phase region should become more narrow as one approaches the Lifshits-type critical point, one may conclude that Rb doping of Cs_2ZnI_4 moves the system away from the singular critical point.

The NQR line shape of Bridgman-grown undoped crystals in the IC phase is in agreement with the spectra of solution-grown crystals with a low Rb concentration. Besides, a comparison of the transition points of undoped crystals grown by the two above methods reveals a shift of the transition temperatures in melt-grown crystals toward higher temperatures for T_i and T_{c1}, and in the opposite direction, for T_{c2}, with respect to pure Cs_2ZnI_4 grown from solution. Melt-grown crystals contain apparently residual impurities in amounts of $0.2-0.4\%$.

Doping results characteristically in a change of the NQR line shape in the IC phase already at the lowest Rb concentration $x=0.0018$ studied. A possible explanation of this observation lies in the presence of order-parameter fluctuations near T_i in the case of a quadratic relation between the resonant frequency and the order parameter, which is valid for the spectrum component II. It was shown, in particular, that

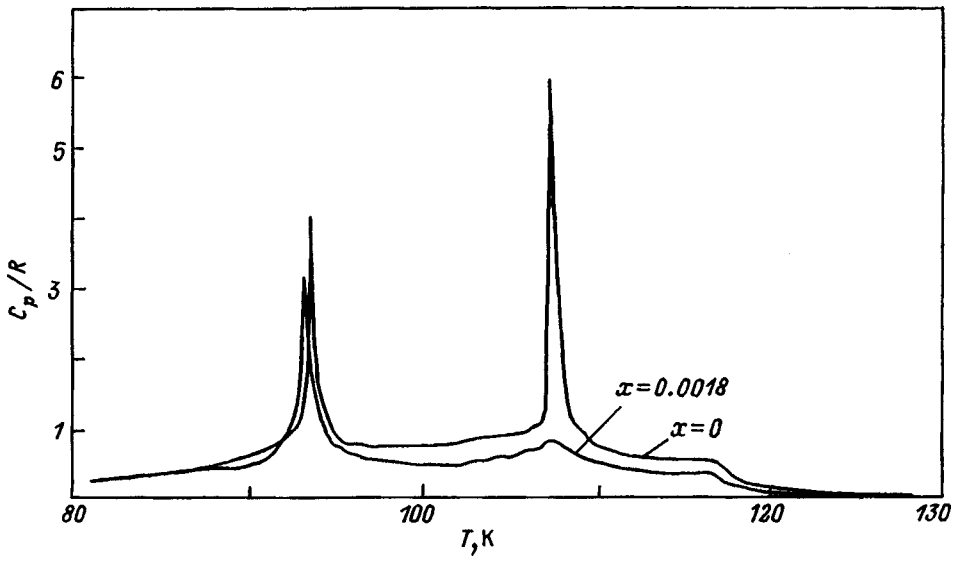

FIG. 5. Temperature dependence of the heat capacity of solution-grown $(Cs_{1-x}Rb_x)_2ZnI_4$ ($x=0$ and 0.0018).

the effect of amplitude fluctuations on the intensity of high-frequency (for Cs_2ZnI_4) side peaks depends essentially on damping, which is characterized by coefficient γ of the dissipation function $[\gamma(\eta_1^2+\eta_2^2)/2]$.[1,6] It is this effect that brings about suppression of the temperature-dependent continuum singularity near T_i in pure Cs_2ZnI_4. If the damping is strong, $\gamma\sim 0.1$,[1] the temperature-dependent side peak can become suppressed to become unobservable against the noise throughout the IC phase interval. Thus the doping-induced change in the spectrum of the IC phase can originate from an increase in fluctuation damping caused by incorporation of the impurity. One cannot exclude also such a ''static'' reason for the variation of the line shape as the onset of several metastable states with fixed values of q_δ. This uncertainty could be removed by studying the temperature dependences of wave vectors q_δ for different impurity concentrations. This requires independent and fairly complex x-ray diffraction measurements which we are planning to perform.

We conclude with the results of a calorimetric study. The fact that even the lowest Rb concentration results in an extremely strong washing out of the thermal anomaly at T_{c1} is apparently a consequence of the well-known formation near the lock-in transition in doped crystals of several modulations having a fairly broad region of coexistence on the side of the IC phase. Note that the peak of the T_{c1} anomaly in the $x=0.0018$ case does not shift with respect to its position in the undoped crystal (Fig. 5), whereas the corresponding transition point derived from NQR data lies higher by 4 K. The fact that the real transition point in doped crystals, rather than coinciding with the thermal-anomaly peak, may sometimes lie substantially higher in temperature was shown, e.g., in Ref. 8.

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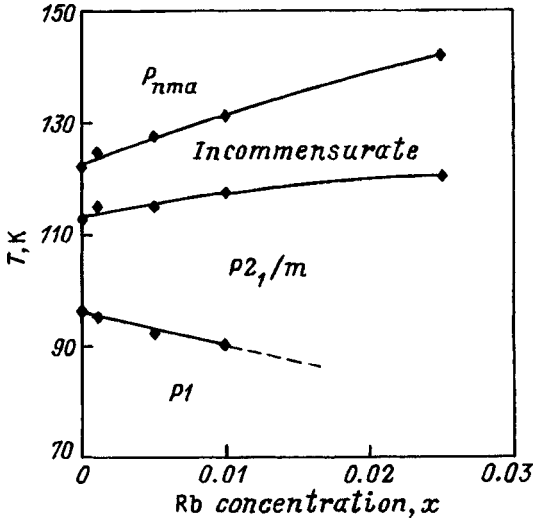

FIG. 6. Phase diagram of the $(Cs_{1-x}Rb_x)_2ZnI_4$ system.

[1] I. P. Aleksandrova, B. Sh. Bagautdinov, J. Bartolomé, R. Burriel, J. Melero, M. A. Popov, and S. V. Primak, Ferroelectrics **169**, 115 (1995).
[2] I. P. Aleksandrova, S. V. Primak, E. V. Shemetov, and A. I. Kruglik, Fiz. Tverd. Tela (Leningrad) **33**, 1344 (1991) [Sov. Phys. Solid State **33**, 758 (1991)].
[3] J. J. Melero, J. Bartolomé, R. Burriel, I. P. Aleksandrova, and S. V. Primak, Solid State Commun. **95**, 201 (1995).
[4] B. Sh. Bagautdinov and I. P. Aleksandrova, Solid State Commun. **90**, 817 (1994).
[5] I. P. Aleksandrova, K. Parlinsky, R. Currat, C. Vettier, and G. Eckold, Ferroelectrics **143**, 17 (1993).
[6] M. A. Popov, I. P. Aleksandrova, and S. V. Primak, JETP Lett. **59**, 485 (1994).
[7] D. G. Sannikov, in *Incommensurate Phases in Dielectrics* (Elsevier, Amsterdam, 1986), edited by R. Blinc and A. P. Levanyuk, Vol. 1, Ch. 2.
[8] J.-G. Yoon, Y. J. Kwag, Y.-S. Cho, and S.-I. Kwun, J. Phys. Soc. Jpn. **62**, 327 (1993).

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