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Investigation of the tricritical point of SbSI by the nuclear quadrupole resonance method

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The rf nuclear quadrupole resonance (NQR) spectroscopy was used for the first time to investigate the critical exponent β and the behavior of the thermodynamic potential near the critical point. Apparatus was assembled and a method was developed for precision NQR measurements when pressure and temperature were altered independently. The behavior of the ferroelectric SbSI near a singularity in the p–T diagram was in full agreement with the behavior of the tricritical point predicted by the Landau theory.

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There have been many theoretical investigations of the behavior of solids near a multicritical point. These investigations have been mainly calculations carried out by the renormalization-group method (see, for example, Refs. 1 and 2). In the case of compounds with a strong exchange interaction this method has made it possible to study states with highly developed fluctuations and to find corrections to the power-law dependences of the various thermodynamic quantities near multicritical points.[3] However, in the case of ferroelectric crystals the range of temperatures where fluctuations of the order parameter are important is much narrower and we can expect the Landau theory[4] to be valid at a critical point.

There have been relatively few experimental investigations because of the complexity of the problem and the need for a high precision of the measurements. In practice, there have been only a few studies carried out at a suitable level. For example, in the case of crystals investigations have been carried out on NH_4Cl (Ref. 5) and measurements of the specific heat at high pressures have been used to study the behavior of the critical exponent α near a tricritical point. A determination of the coefficients of the thermodynamic potential of potassium dihydrogen phosphate near its tricritical point was reported in Ref. 6. The permittivity of barium titanate was measured in the vicinity of a singular point.[7] Similar investigations have been made of metamagnetic materials.[8] A study of the critical exponent α of SbSI near a singular point in the p–T diagram was published[9] when the present paper was being prepared for press.

As a rule, the critical exponents have been determined from the temperature dependences of the relevant macroscopic quantities. More recently, studies of the influence of temperature on the order parameter have become concentrated on "microscopic" methods which can give very precise values of the atomic displacements or of the microparameters associated directly with them. Neutron diffraction has been used successfully,[10,11] but it is very difficult to combine this method with the application of high pressures. Radiofrequency (rf) spectroscopic methods have been used with success for some time in studies of the temperature dependences of the order parameters.[12-14] We can therefore assume that it should be possible to use rf spectroscopic methods in investigations of multicritical points. This is a promising approach because it is simpler and easier to apply high pressures in these methods than in the diffraction techniques. In studies of this kind one needs a system which can detect quadrupole resonance signals in a high-pressure chamber and provides means for varying independently and maintaining with the required precision two parameters: the pressure q and the temperature T.

Our aim was to assemble suitable apparatus, develop a measurement method, analyze statistically the results of a precision determination of the critical exponent β, and make specific studies near the critical point in the p–T diagram of the ferroelectric SbSI. We found the critical exponent β of the order parameter and studied the behavior of the coefficients of the thermodynamic potential in different parts of the p–T diagram.

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EXPERIMENTAL METHOD

The nuclear quadrupole resonance (NQR) frequencies of the ^{121}Sb and ^{123}Sb isotopes were measured using a standard ISSh-1-12 spectrometer. Two lines of ^{121}Sb ($I = 5/2$), corresponding to transitions between the energy levels of the quadrupole interaction, were used mainly in high-pressure measurements. The quadrupole coupling constant e^2Qq and the asymmetry parameter η of the antimony nuclei in SbSI were calculated by tabulating the eigenvalues of the energy in the quadrupole Hamiltonian, considered as a function of the asymmetry parameter, in steps of η amounting to 0.001. The constant e^2Qq was determined to within 0.05%. A sample was placed in a high-pressure chamber made of beryllium bronze of the BR-B2 type. The construction of the chamber with special low-capacitance terminals, capable of withstanding voltages up to 2.5 kV in an rf pulse, was similar to that described in Ref. 15. A special system with oppositely directed streams of a cooling agent eliminated practically completely the temperature gradient along a sample (to within 0.01 °K). The temperature of the cooling agent was maintained to within at least ±0.03 °K. Before measurements at any point the temperature was stabilized for 30–40 min. This temperature was measured with a monolithic copper–Constantan thermocouple introduced through a special seal; the thermocouple was calibrated using a TSPN-1 platinum resistance thermometer. Measurements of the absolute temperature were accurate to within 0.1 °K. The pressure inside the chamber was measured with a Manganin transducer whose pressure coefficient was determined by comparison with a standard manometer calibrated at the All-Union Scientific-Research Institute of Physicotechnical and Radio Engineering Measurements. The resistance of the pressure transducer and the thermoelectric power were measured with high-precision (0.002 class) potentiometers.

The apparatus ensuring the creation and maintenance of pressure in a chamber was described in detail in Ref. 16 and it consisted of a pressure booster and of a pump unit which made it possible to vary the pressure continuously. The pressure was maintained to within ±10 bar. The pressure-transmitting medium was an oil–pentane mixture.

Samples of SbSI, kindly supplied by V. A. Lyakhovitskaya, were grown from the melt and were in the form of textured blocks with a preferential crystallite orientation along the c axis coinciding with the direction of spontaneous polarization. The samples selected for our study were those for which the NQR signal was narrowest.

EXPERIMENTAL RESULTS

Figure 1 shows the isobaric temperature dependences of e^2Qq obtained at nine pressures p from atmospheric to 2 kbar. At atmospheric pressure the behavior of e^2Qq and η was typical of the first-order phase transitions, as reported earlier in Ref. 17. In the region of ~2.5 °K near the phase transition point T_0 the spectrum was that of a two-phase system composed of lines due to the original and ferroelectric phases. Cooling in this range reduced the intensities of the lines of the original phase and increased the intensities of the lines of the new phase. The temperature hysteresis amounted to 0.2 °K.

When the pressure was increased, the phase transition temperature decreased linearly at a rate of $dT_c/dp = -38$ °K/kbar to $p = 1.5$ kbar and then the dependence became nonlinear. The jump of e^2Qq at T_0 decreased on increase in the pressure and practically disappeared at $p = 1.4$ kbar. At this pressure the two-phase region extended over just 0.3 °K. Increase in the pressure also gradually reduced the width of the temperature hysteresis region. At $p_{cr} = 1.5$ kbar ($T_{cr} = 231.45$ °K) the behavior of e^2Qq and η was typical of continuous phase transitions.

The change in the nature of the phase transition in SbSI under pressure was first deduced from optical

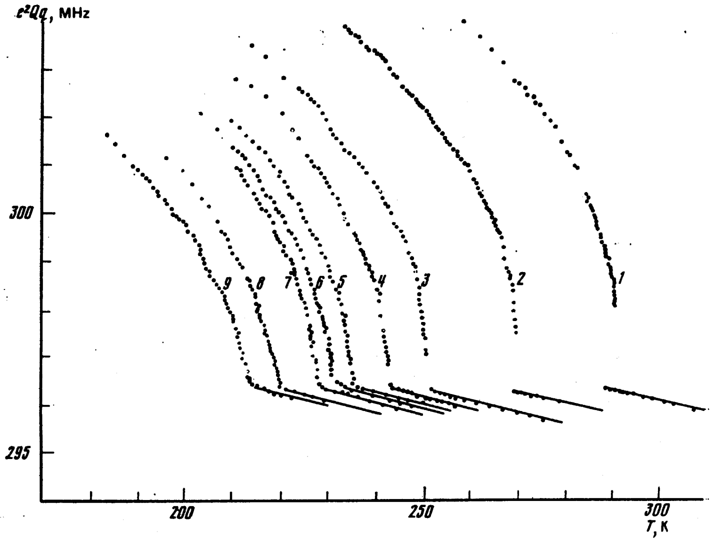

FIG. 1. Isobaric temperature dependences of the quadrupole constant e^2Qq of the ^{121}Sb nuclei in SbSI at the following pressures: 1) 1 atm; 2) 0.5 kbar; 3) 1.0 kbar; 4) 1.2 kbar; 5) 1.4 kbar; 6) 1.5 kbar; 7) 1.6 kbar; 8) 1.8 kbar; 9) 2.0 kbar. The lines represent the behavior of e^2Qq in the paraelectric phase.

and dielectric measurements in Ref. 18, where the critical values $p_{cr} = 1.5$ kbar and $T_{cr} = 233\,^\circ$K were reported.

DETERMINATION OF THE CRITICAL EXPONENT OF THE ORDER PARAMETER

The electric-field gradient q_{ij} in the low-temperature phase can be described by a series expansion in terms of powers of the displacements from equilibrium positions (in the original phase) of those ions which participate in the soft vibration mode[12]:

$$q_{ij}=q_{ij}^0+\sum_l K_l\varphi_l+\sum_l L_{ll}\varphi_l^2, \tag{1}$$

where q_{ij}^0 is the corresponding component of the electric-field gradient tensor for the original phase; K_l and L_{ll} are the coefficients in the Taylor series

$$K_l=\frac{\partial q_{ij}}{\partial \varphi_l},\quad L_{ll}=\frac{\partial^2 q_{ij}}{\partial \varphi_l^2},$$

and l is the coordinate of an atom in the lth position.

It is known[19] that the Sb ions are "ferroelectrically active," i.e., their displacements from the equilibrium positions determine mainly the appearance of the spontaneous polarization in the low-temperature phase and in the case of SbSI this polarization is a macroscopic order parameter P. We can then rewrite Eq. (1) in the form

$$q_{zz}=q_{zz}^0+aP+bP^2, \tag{2}$$

where a and b are certain constant coefficients. Depending on the symmetry of the position of a given nucleus in the original phase, we can expect Eq. (1) to be dominated by the linear or quadratic (in the displacements) term.

The coefficients of the expansion (1) are usually determined by calculating the lattice sums in the point-ion approximation. However, in the case of SbSI such calculations do not give the correct result. Even inclusion of the dipole contribution in the calculations of the electric-field gradient fails to ensure agreement with the experimental values of this gradient at the antimony nuclei.[20] Therefore, the linear and quadratic approximations were checked. It was established in the first case[21] that near a phase transition at pressures $p > 1.4$ kbar the critical exponent of the order parameter is almost twice as large as $\beta = 0.5$. Therefore, we adopted the approximation

$$(e^2Qq_{zz}-e^2Qq_{zz}^0)=\Delta e^2Qq\sim bP^2. \tag{3}$$

The temperature dependence of Δe^2Qq below T_0 was governed by the temperature dependence of the order parameter P and was approximated by a simple power function $\Delta e^2Qq = A\varepsilon^{2\beta}$, where $\varepsilon = (T_x - T)/T_x$. The value of β in the logarithmic dependence $\ln(\Delta e^2Qq)^{1/2} \sim \beta \ln\varepsilon$ was found by the method of least squares and T_x was regarded as the variable parameter. At pressures below p_{cr} the values of T_x agreed (within the limits of the empirical error) with the experimental values of the phase transition temperature T_0. It was possible to reduce the number of points on the high or low temperature side. On the average, a total of about 50 points was used for each isobar. The anomalous part of Δe^2Qq was separated by extrapolating the linear high-temperature dependence toward low temperatures and the parameters of this dependence were determined by the least-squares method.

Figure 2 shows the behavior of the order parameter at pressures from 1.5 kbar up. Table I gives the values of β in the temperature range where $\ln(\Delta e^2Qq)^{1/2}$ is a linear function of $\ln\varepsilon$. At 1.5 kbar we found that $\beta = 0.27 \pm 0.03$ throughout the temperature range up to T_0 (the confidence interval corresponded to 95% probability). Already at 1.6 kbar the linear part of the isobar corresponded to $\beta = 0.47 \pm 0.03$ and both in the direct vicinity of T_0 as well as at lower temperatures there were regular deviations from linearity. On increase in pressure the range where $\beta = 0.5$ became greater.

We also determined the value of the index β in a coordinate system formed by the tangent and normal to the phase transition line at the critical point. Along the normal to the phase transition line in the $p-T$ diagram the value of β was exactly 1/4.

INVESTIGATION OF THE BEHAVIOR OF THE THERMODYNAMIC POTENTIAL

We shall write the thermodynamic potential including a term with the sixth power of the order parameter[22]:

$$\Phi=\Phi_0+AP^2+BP^4+CP^6. \tag{4}$$

This potential is suitable also for the analysis of the first-order phase transitions near the critical point.[4,23]

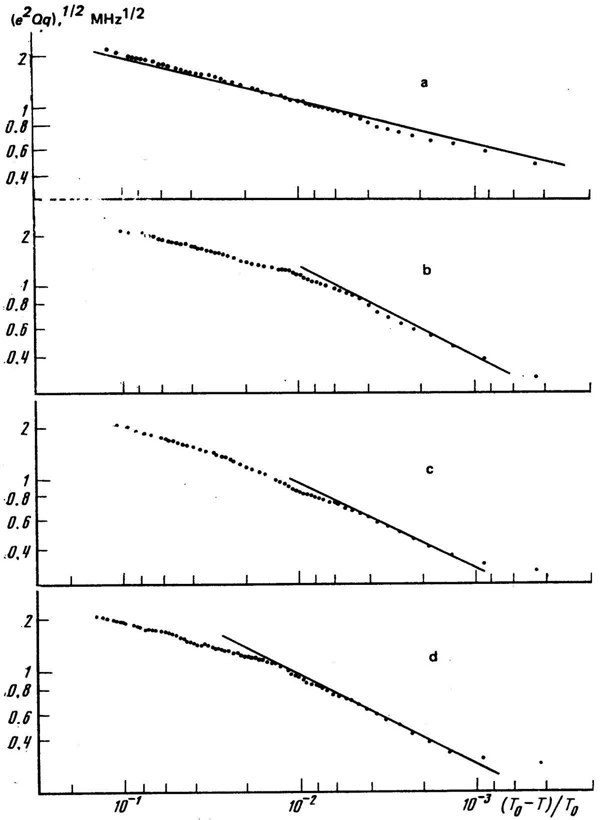

FIG. 2. Behavior of the anomalous contribution Δe^2Qq associated with the order parameter in the region of continuous phase transitions: a) 1.5; b) 1.6; c) 1.8; d) 2.0 (pressures in kilobars). The straight lines correspond to $\beta = 0.25$ at $p = 1.5$ kbar and $\beta = 0.5$ at all higher pressures $p > 1.5$ kbar.

TABLE I. Values of critical exponents β in critical and transcritical regions.

Pressure, kbar	Value of β	Range of validity, °K	Pressure, kbar	Value of β	Range of validity, °K
1,5	0.27±0,03	$0.1 \leqslant T_0 - T < 26$	1.8	0.51±0,02	$0.3 \leqslant T_0 - T \leqslant 1.5$
1,6	0,47±0.03	$0.3 \leqslant T_0 - T \leqslant 1$	2.0	0.48±0.03	$0.3 \leqslant T_0 - T \leqslant 3$

In the expansion (4), within an isobar, the value of A is assumed to vary linearly with temperature, B and C are taken to depend weakly on T, and it is assumed that $C > 0$. It is convenient to write the order parameter as a function of A, B, C, and T_c in the form

$$P^2 = \frac{-B + [B^2 - 3A_0(T - T_c)C]^{1/2}}{3C}. \tag{5}$$

In Fig. 3 the values of B/A_0 and C/A_0 are obtained as parameters of the straight line[23] and can be calculated by the least-squares method. The results of such calculations are presented in Table II, which includes also the experimental values of the transition temperature T_0. It is clear from this table that the coefficient B changes its sign and passes through zero near the critical point. Calculations of the errors of the quantities listed in Table II were carried out by expanding as a series in terms of all the unknown parameters near the principal minimum of the variation of the parameters. The error did not exceed ±0.2 for the ratio B/A_0 and ±0.1 for the ratio C/A_0.

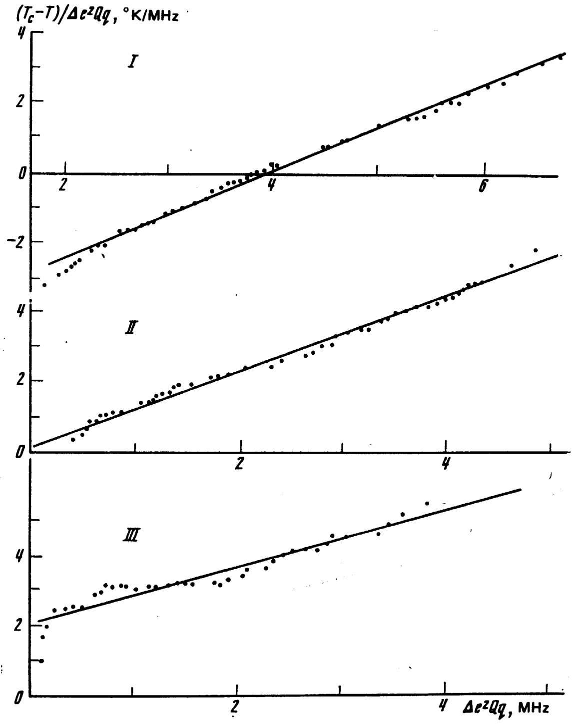

FIG. 3. Determination of the coefficients of the thermodynamic potential described by Eq. (4) from the temperature dependence of Δe^2Qq at three different pressures: I) first-order phase transition ($p = 1$ atm); II) critical point ($p = 1.5$ kbar); III) continuous phase transition ($p = 1.8$ kbar). The parameters of the continuous lines are given in Table II.

TABLE II. Values of coefficients of thermodynamic potential calculated from temperature dependence of Δe^2Qq at various pressures.

Pressure, kbar	B/A_0	C/A_0	T_c, K	T_0, K
0.001	−2.6	0,4	284.75	288.45
0.5	−1.7	0.4	267,15	268.75
1.0	−1.1	0.4	249.95	250,25
1.2	−0.2	0.3	242.95	243.25
1,4	−0.03	0.3	235.45	235.65
1.5	+0,02	0.4	231.45	
1.6	+0.3	0.3	228.45	
1.8	+1.1	0.3	220.65	
2.0	+1.0	0.4	214.15	

DISCUSSION OF RESULTS

It is clear from Tables I and II that the description of the behavior of SbSI near a singular point in the $p-T$ diagram is in full agreement with the behavior of a tricritical point in the Landau theory.[4] A critical point of the same order follows from a study of the thermal expansion of SbSI reported in Ref. 9.

It is worth noting that on closest approach to a tricritical point the Landau theory is obeyed at all temperatures up to those separated from T_0 by an amount equal to the experimental error in the determination of temperature (0.1 °K). Near second-order transitions close to T_0 there are regular deviations from the classical exponent $\beta = 0.5$, which becomes smaller. Unfortunately, the origin of these deviations is not clear because the precision reached in our experiments and the pressures attained (which were the highest for liquid-type chambers) were insufficient for a detailed investigation of the range $T_0 - T < 0.1$ °K.

The low-temperature deviations from linearity in Fig. 2 can be attributed to the presence of the term with the sixth power of the order parameter in the thermodynamic potential.[4] The influence of this term gradually decreases as we move away from the tricritical point to the region of the second-order transitions and this is due to an increase in the coefficient in front of the fourth power of the order parameter.

In principle, the temperature resolution (accuracy in the measurements) reached in our experiments does not represent the maximum attainable in rf investigations under pressure and, therefore, it should be possible to determine the critical exponent more accurately. Moreover, methods of this kind can be used to investigate any structural transition and this should make it possible to study the behavior of the order parameter even in those cases when the macroscopic parameter cannot be measured for one reason or another.

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Submillimeter dielectric spectra of Rochelle salt

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Submillimeter monochromatic spectroscopy in the frequency range 3–13 cm^{-1} and in the temperature interval 180–300 K were used to measure the dielectric spectra $\varepsilon^*(\nu,T)$ of Rochelle salt. It is shown that the singularities observed in the spectra are a continuation of the fundamental ferroelectric dispersion observed earlier at lower frequencies. It is established that in the low-temperature antipolar phase the reciprocal relaxation time obeys a cubic temperature dependence that is rather unusual for most ferroelectrics.

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1. INTRODUCTION

Phase transitions in Rochelle salt—the first known ferroelectric—have been comprehensively investigated for several decades, but some aspects of these phenomena and of the associated processes remain still debatable. No thorough investigation has been made, in particular, of the porlaization mechanisms that produce in the crystal, in a certain temperature interval (255–297 K), a state with spontaneous polarization.[1] As applied to this problem, the most informative experimental method turned out to be dielectric spectroscopy. At the frequencies 10^9–10^{11} Hz, the dielectric spectra of Rochelle salt have a clearly pronounced singularity in the form of a broad and rather intense absorption line, whose properties depend on temperature. The temperature behavior of this low-frequency (compared with the usual lattice vibrations) mode changes radically at the phase-transition points, and there is no doubt that it is most closely connected with the ferroelectric properties of the Rochelle salt.[2]

The study of the frequency and temperature dependences of the dielectric constant $\varepsilon^*(\nu, T)$ of this crystal has long been carried out practically simultaneously with the development and evolution of the necessary experimental procedures. Consequently some understanding of the character of the dispersion of $\varepsilon^*(\nu, T)$ was gained only in the early Seventies, when practical procedures were developed for the measurement of anomalously high values of the dielectric parameters of materials at radio and microwave frequencies. The $\varepsilon^*(\nu, T)$ dependences obtained for Rochelle salt[2] have become the classical example of relaxation dispersion of the dielectric constant in ferroelectrics. These dependences were the basis for the determination of the parameters of ferroelectrically active excitation of a crystal and of the determination of their temperature dependences near the phase transition points.

The present study followed the general plan of the investigation of the dielectric properties of ferroelectrics in the submillimeter band. Its purpose was the measurement of the temperature dependences of the real (ε') and imaginary (ε'') parts of the dielectric constant of Rochelle salt along the ferroelectric axis at frequencies ~10 cm^{-1} (3×10^{11} Hz). From the point of view of the study of the ferroelectric mode, this expansion of the region of the investigation of the dispersion of $\varepsilon^*(\nu, T)$ is of interest, since it can provide a better idea of the temperature dependence of the parameters of this mode the hitherto prevailing notion based on RF

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