Investigation of phase transitions in iron orthoborate in the vicinity of the Néel point

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An investigation was made of the Mössbauer spectra of a single crystal of iron orthoborate (Fe_3BO_6) near the Néel temperature in zero external field and in a field directed along the [b] and [c] axes of the crystal. The critical exponents of the inequivalent c and d sublattices of Fe_3BO_6 were determined in the temperature range $2\times10^{-3} \leq (T-T_N)/T_N \leq 8\times10^{-2}$: $\beta_c = 0.350\pm0.007$; $\delta_c = 4.46\pm0.10$; $\beta_d = 0.352\pm0.005$; $\delta_d = 4.42\pm0.08$. A simultaneous comparison of the β exponents of iron borate and various materials with different types of magnetic anisotropy demonstrated that the experimental values of β were in agreement with the results of calculations carried out using the renormalization-group theory of phase transitions.

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INTRODUCTION

The asymptotic behavior of the thermodynamic properties of magnetically ordered systems in the vicinity of the critical point where $t=(T-T_c)/T_c \to 0$ has been investigated quite thoroughly by the theoretical renormalization-group method.[1] The results predict a dependence of the critical exponents on the number of dimensions of d of the lattice and the number of components n of the order parameter, which are governed by the magnitude and nature of the magnetic anisotropy. However, the experimental studies of the critical exponents are always carried out at temperatures corresponding to $t \neq 0$. For this case the theory[2,3] predicts a crossover transition of the critical behavior under the influence of the magnetic anisotropy from isotropic ($n=3$) to planar ($n=2$) or Ising ($n=1$) on approach to T_c. This transition occurs at a crossover temperature $t_{co} \approx (H_A/H_E)^{1/\phi}$, where H_A and H_E are the effective anisotropy and exchange fields, respectively, and $\phi(n)$ is the critical crossover exponent.

It would be interesting to check experimentally these predictions of the theory of phase transitions by considering magnetic materials with different types of anisotropy. The problem is that the available experimental data have been obtained mainly for critical exponents of simple magnetic systems exhibiting pure Ising or Heisenberg behavior. The critical properties of complex many-sublattice magnetic materials, particularly antiferromagnets with the Dzyaloshinskiĭ interaction, have not yet been investigated sufficiently thoroughly. Such systems can be studied conveniently by the Mössbauer spectroscopy method because the hyperfine fields at the nuclei of atoms located in different sublattices are usually proportional to the magnetization of the sublattice in which they are located. We shall report a Mössbauer spectroscopic investigation of the critical behavior of a weak ferromagnet (iron orthoborate Fe_3BO_6) exhibiting the orthorhombic magnetic anisotropy.

The critical behavior of this substance has already been investigated by Kamzin, Bokov, and Smolenskiĭ[4] who used the Mössbauer method and found that the critical exponents β_c, δ_c and β_d, δ_d of the magnetization of the inequivalent c and d sublattices were very different. These indices differed greatly also from the values of β and δ obtained by Voigt and Roos[5] from the magnetic measurements. Moreover, Kamzin and Bokov[6] observed coexistence of the paramagnetic and ordered phases in a wide range of temperatures below the Néel point T_N on application of a magnetic field along the [b] axis of a crystal but they provided no satisfactory explanations of this effect. Therefore, it seemed essential to carry out a more detailed study of the behavior of the magnetizations of the iron orthoborate sublattices near T_N in the absence of an external field and also in fields directed along different axes of a crystal of this substance.

EXPERIMENTAL PROCEDURE

A single-crystal rectangular place of Fe_3BO_6 of $5\times2\times0.08$ mm dimensions was used as the Mössbauer absorber. The directions of the crystal axes [b] and [c] coincided with the sides of the plate, whereas the [a] axis and the direction of the gamma-ray beam were perpendicular to the plane of the plate. This plate was located in a high-temperature oven, whose construction made it possible to rotate the investigated sample about the [a] axis through a given angle with an error not exceeding 1°. An external field was parallel to the plane of the plate. The Mössbauer measurements were carried out using a NOKIA LP-4840 multichannel analyzer and a single-channel spectrometer operating at a constant velocity of the source (Co^{57} in a rhodium matrix). The Mössbauer spectra were analyzed on a BÉSM-6 computer by the least-squares method using a program described by Nikolaev, Rusakov, and Yakimov.[7] The temperature of the sample was kept constant to within 0.03 °K. The temperature drop along the sample was of the same order of magnitude. The Néel point deduced by the scanning method was $T_N = 507.30\pm0.05$ °K.

RESULTS

Several investigations (see, for example, Ref. 8) have shown that the unit cell of Fe_3BO_6 contains twelve Fe^{3+} ions occupying two inequivalent crystallographic positions 8d and 4c. The moments of the iron ions at positions of the same type form two antiparallel sub-

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lattices whose magnetizations deviate slightly from the common axis because of the Dzyaloshinskiĭ interaction. Thus, the magnetic properties of iron orthoborate can be described by a four-sublattice model and for each pair of sublattices we can introduce the following ferromagnetic and antiferromagnetic vectors:

$$\mathbf{m}_i=(\mathbf{M}_{1i}+\mathbf{M}_{2i})/2M_{0i}, \quad \mathbf{l}_i=(\mathbf{M}_{1i}-\mathbf{M}_{2i})/2M_{0i}, \quad i=d,\ c.$$

Below the spontaneous spin reorientation temperature ($T_{sp1}=415$ °K) the orientations are $\mathbf{m}_f \| [a]$ and $\mathbf{l}_f \| [c]$, whereas at temperatures $T_{sp1} < T < T_N$ the orientations are $\mathbf{m}_f \| [c]$ and $\mathbf{l}_f \| [a]$. Moreover, according to Kamzin and Bokov,[9] the moments of the 4*c* ions deviate from the [*a*] to the [*b*] axis above $T_{sp2} \approx 490$ °K.

1. Measurements in a field H || [*b*]

Kamzin and Bokov[6] found that at $T < T_N$ the application of an external field $\mathbf{H} \| [b]$ produces, against the background of the split Zeeman spectra corresponding to the antiferromagnetic state of the sample, additional absorption lines in the center of the spectrum and the positions of these lines coincide with the positions of the quadrupole splitting lines of the paramagnetic phase. This anomaly has not yet been observed in antiferromagnets of this type subjected to transverse fields.

We determined the mechanism of this effect by investigating the Mössbauer spectra of iron orthoborate in external fields up to 27 kOe in the same temperature range. All the spectra had the same form and some of them are shown in Fig. 1 (for comparison, the lower part of this figure shows the spectrum obtained in the absence of an external field). We can see that these spectra have no lines corresponding to the paramagnetic state. An analysis of the spectra on a computer confirmed that they represent a superposition of two (*c*, *d*) Zeeman sextets with the intensity ratio $I_{8d}:I_{4c} \approx 2:1$, in agreement with the distribution of the iron ions between the sublattices.

The sensitivity of the effect discovered in Ref. 6 to the angle θ between H and [*b*] was studied by recording the spectra also at $T-T_N=-5$ °K in a field of $H=27$ kOe in an angular range $\theta=\pm 10°$ where measurements were carried out in steps of 1°. None of these spectra showed the paramagnetic phase lines. On the other hand, a transition to the disordered state occurred in an external field as abruptly as in $H=0$. This made it possible to use the temperature scanning method to investigate the dependence of the shift of the transition on the field, which amounted to 0.6 ± 0.1 °K in a field $H=27$ kOe.

2. Measurements in fields H = 0 and H || [*c*]

Bayukov, Ikonnikov, and Petrov[10] used the Mössbauer spectroscopy method to determine the asymmetry parameters and the orientations of the principal axes of the electric-field gradient (EFG) tensors at the ^{57}Fe nuclei and the 8*d* and 4*c* positions (these orientations were determined relative to the crystal axis of iron orthoborate). The quadrupole splittings deduced from the spectra in the $T > T_N$ range were $\Delta E_Q(8d)=0.58$ mm/sec and $\Delta E_Q(4c)=1.13$ mm/sec, respectively.

The Zeeman splitting of the excited nuclear sublevels $\Delta E_H(I=3/2)$ in the spectra determined at $T < T_N$ (one of them is shown at the top of Fig. 2) was found to be comparable with the quadrupole splitting ΔE_Q in the temperature interval $t < 10^{-1}$. Therefore, in calculating the hyperfine field H_{hf} from the experimentally determined splitting H_{exp} of the spectra an allowance was made for the additional line shifts calculated in Refs. 11 and 12. Since the corrections for these shifts increased in the ratio $y=2\Delta E_H/\Delta E_Q$ and since in the investigated temperature range it was found that $y(8d):y(4c) \approx 2:1$, these corrections for the iron nuclei at the 4*c* positions were greater than for the 8*d* positions. A similar situation has been encountered already in an analysis of the behavior of the magnetizations of the *a* and *b* sublattices of yttrium iron garnet ($Y_3Fe_5O_{12}$) near T_c (Ref. 13).

One of the spectra obtained in an external field parallel to the easy ferromagnetic axis [*c*] at the Néel point is shown in the lower part of Fig. 2. We can see that the application of a magnetic field induces different ef-

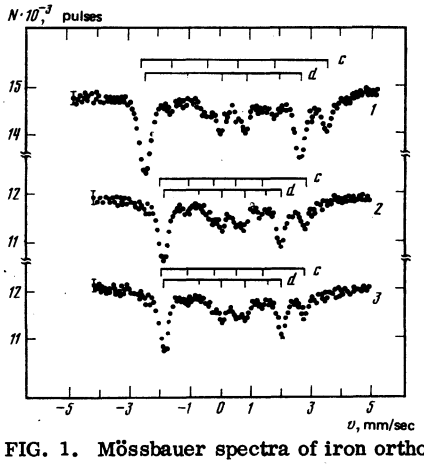

FIG. 1. Mössbauer spectra of iron orthoborate in a field $\mathbf{H} \| [b]$: 1) $H=27$ kOe, $T-T_N=-10.6$ °K; 2) $H=27$ kOe, $T-T_N=-5$ °K; 3) $H=0$, $T-T_N=-5$ °K.

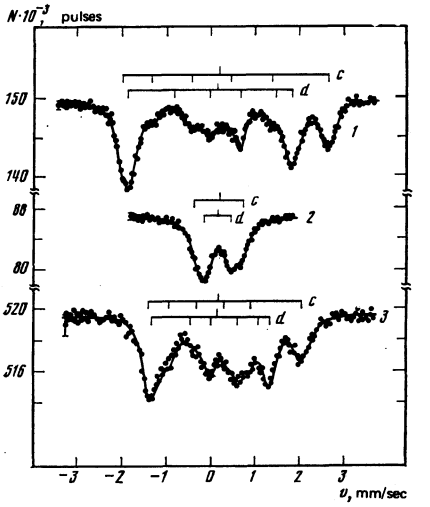

FIG. 2. Mössbauer spectra of Fe_3BO_6 near T_N: 1) $H=0$, $T-T_N=-4.1$ °K; 2) $H=0$, $T=T_N$; 3) $H=27$ kOe, $T=T_N$ ($\mathbf{H} \| [c]$).

fective fields at the iron nuclei in the d and c sublattices, as found earlier by Kamzin and Bokov.[14]

As in the $H=0$ case, the effective field H_{eff} was determined allowing for the corrections to H_{exp} and the hyperfine field was calculated from

$$H_{hf}=(H_{eff}^2-H^2)^{1/2}.$$

The critical parameters of each sublattice were determined from the experimental data using

$$\bar{H}_{hf\,i}(T,H)=H_{hf\,i}(T,H)/H_{hf\,i}(0,0)=l_i(T,H)$$

(i.e., assuming proportionality of the hyperfine field to the sublattice magnetization) and applying the least-squares method by means of the formulas

$$l(T,0)=B(-t)^{\beta}, \quad t=(T-T_N)/T_N,$$
$$l(0,H)=D(\bar{H})^{1/\delta}, \quad \bar{H}=g\mu_B SH/kT_N. \tag{1}$$

The range of asymptotic critical behavior was determined more accurately by varying initially only β_i and B_i and taking T_N to have a fixed value found experimentally. Next, the dependence of β_i on the upper limit t_m of the temperature interval was plotted and this was used to determine the range of asymptotic behavior where β_i was stabilized near some average value. In this region the results were analyzed again varying the value of T_N. The results of this analysis show that the critical exponents of different sublattices of iron orthoborate were practically identical: $\beta_d=0.352\pm0.005$ and $\beta_c=0.350\pm0.007$ in the temperature interval $2\times10^{-3}<t<8\times10^{-2}$. The calculated value $T_N=507.28\pm0.02$ °K was in good agreement with the value T_N found experimentally by the scanning method. The exponents of the critical isotherm also had very close values: $\delta_d=4.42\pm0.08$ and $\delta_c=4.46\pm0.10$.

It was interesting to compare our results with those of Ref. 4, where an attempt was also made to determine the critical exponents of Fe_3BO_6 by the Mössbauer method but "splitting" of their values was observed: $\beta_d=0.332$ and $\beta_c=0.287$; $\delta_d=4.6$ and $\delta_c=5.1$. Figures 3 and 4 show the dependences $l_i(t,0)$ and $l_i(0,\bar{H})$ on logarithmic scales. The dashed lines give the same dependences deduced from an analysis of our data without inclusion of the corrections to H_{exp}. It is clear from

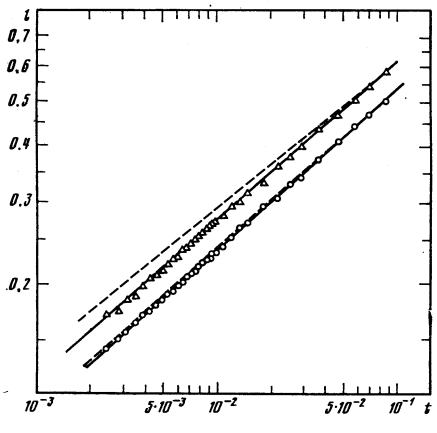

FIG. 3. Temperature dependences of the reduced sublattice magnetizations of Fe_3BO_6: triangles represent the c sublattice and the circles—the d sublattice. The dashed lines are drawn without allowance for the corrections to H_{exp}.

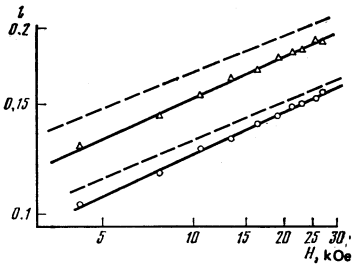

FIG. 4. Critical isotherms of the iron orthoborate sublattices: triangles represent the c sublattice and the circles—the d sublattice. The dashed lines are plotted without allowance for the corrections to H_{exp}.

these figures that allowance for these corrections effectively suppresses the splitting of the critical exponents: $\beta_c=\beta_d=\beta=0.351\pm0.006$ and $\delta_c=\delta_d=\delta=4.44\pm0.10$. These values are close to $\beta=0.347\pm0.006$ and $\delta=4.6\pm0.3$ found by Voigt and Roos[5] from magnetic measurements.

DISCUSSION

According to the theoretical ideas,[2,3] the influence of the magnetic anisotropy on the critical behavior of magnetic materials is manifested by a reduction in the dimensionality of the order parameter from n to $m<n$ in the temperature range $t<t_{co}$. Thus, if the crossover temperature $t_{co}\approx(H_A/H_E)^{1/\Phi}$ lies in the asymptotic region, the critical behavior at temperatures $t<t_{co}$ and $t>t_{co}$ corresponds to different classes m each of which is described by its own set of critical exponents β for a number of ferromagnets, ferrimagnets, and antiferromagnets (Table I) and compare them with the results of calculations carried out using different approximations in the renormalization-group theory of phase transitions (Table II). Table I gives data on only those compounds for which the behavior of the order parameter has been studied by observing the hyperfine interaction and the experimental results have been analyzed by the same method described in subsection 2 in the preceding section. This is a very important point because the method of determination of the phase transition temperature and the range of asymptotic behavior have a strong influence on the precision of determination of β (Refs. 13, 15, and 16). The results for nickel and iron, and those for iron and manganese fluorides are taken from the work of Suter and Hohenemser.[17]

It is clear from Table I that in the classification of the values of β we can identify three ranges: 1) 0.33

TABLE I. Critical exponent β (experimental values).

Substance	β*	Measurement method**	Reference	Substance	β*	Measurement method**	Reference
$Y_3Fe_5O_{12}$	0.39(1)	MS	[13]	$YFeO_3$	0.36(1)	MS	[25]
Ni	0.385(5)	γ–γ	[17]	FeF_3	0.352(6)	MS	[17]
Fe	0.379(4)	MS	[17]	Fe_3BO_6	0.361(6)	MS	our results
$FeBO_3$	0.37(1)	MS	[13]	MnF_2	0.333(3)	NMR	[17]
α-Fe_2O_3	0.365(7)	MS	[15]	FeF_2	0.33(1)	NMR	[17]

*The values in parentheses are the errors in the last significant figure of the index.

**Here, MS denoted Mössbauer spectroscopy, $\gamma-\gamma$ is the method of perturbed angular gamma–gamma correlations, and NMR is the nuclear magnetic resonance method.

TABLE II. Critical exponent β (theoretical values).

	$n=1$	$n=2$	$n=3$
εExpansion (including terms up to $\sim\varepsilon^2$) (Ref. 22)	0.34	0.36	0.38
Solution of renormalization-group equations in real ($d=3$) space (Ref. 23)	0.325	0.346	0.365
Numerical solution of renormalization-group equations (Ref. 24)	0.337	–	–

$\leqslant\beta\leqslant 0.34$; 2) $0.35\leqslant\beta\leqslant 0.37$; 3) $0.38\leqslant\beta\leqslant 0.39$. The exponents of the compounds lying within the same range are clustered around the average value $\bar{\beta}$. For example, in the case of MnF_2 and FeF_2, we have $\bar{\beta}_1=0.332$, whereas in the case of $FeBO_3$, α-Fe_2O_3, $YFeO_3$, and FeF_3 we have $\bar{\beta}_2=0.362$, while for Fe, Ni, and $Y_3Fe_5O_{12}$ we find that $\bar{\beta}_3=0.384$. A comparison of the average experimental values with the calculated values $\beta(n)$ in Table II shows that $\bar{\beta}$ is much closer to the result of calculations carried out using the ε-expansion method (in the second order in respect of ε) than to the results obtained by solving the renormalization-group equations in real ($d=3$) space. The exceptions to this rule are the values of $\bar{\beta}_1$ which are equally close to all the calculated $\beta(n=1)$ results. However, in our case it is more important that the differences $\Delta\beta\approx 0.02$–0.03 are in good agreement with the calculated differences $\Delta\beta(n)=0.02$, because the latter are the same in both theoretical methods. Hence, we can conclude that compounds whose indices lie in the same range belong to one class.

Estimates of the crossover temperature for magnetic materials in the third class give values t_{co} for the crossover from $n=3$ to $m=2$ $[t_{co}(3\to 2)]$ which are two or three orders of magnitude smaller than the lower limit of the temperature region where β is investigated. For example, in the case of cubic ytrrium iron garnet we have $t_{co}\approx 10^{-6}$ so that the temperature interval $10^{-3}<t<10^{-2}$ of variation of β of this substance is entirely within the region of isotropic critical behavior.[13] Similarly, a uniaxial antiferromagnet FeF_2 belonging to the first class exhibits the Ising critical behavior in the range $5\times 10^{-4}<t<7\times 10^{-2}$ which is below $t_{co}\approx 2\times 10^{-1}$ for the crossover from $n=3$ to $m=1$ $[t_{co}(3\to 1)]$.

In contrast to the materials in the third class, we find that estimates of the crossover temperature for the second and first (for example, MnF_2) classes obtained for $t_{co}(3\to 2)$ and $t_{co}(3\to 1)$ lie within the range where β is determined. However, these estimates are only approximate and different situations may occur. For example, Ikeda[18] reports that the $(3\to 2)$ crossover in the critical behavior of the specific heat of an easy-plane antiferromagnet $CsMnF_3$ is found experimentally at $t_{co}\approx 2\times 10^{-2}$, whereas estimates give $t_{co}\approx 3\times 10^{-2}$. Moreover, the crossover itself in real crystals is a gradual process and it may extend over a considerable temperature interval. This applies to the critical behavior of the specific heat of a uniaxial antiferromagnet MnF_2 for which the estimate gives $t_{co}\approx 5\times 10^{-3}$ and the $(3\to 1)$ transition occupies the interval $10^{-3}<t<10^{-2}$ (Ref. 19).

The critical exponent β found by us for the orthorhombic crystal of Fe_3BO_6 lies, within the investigated temperature range, in the region of planar behavior. According to Refs. 4 and 20, iron orthoborate can be regarded as an Ising antiferromagnet in this range. In fact, this compound exhibits close to T_N two reorientation points T_{sp1} [which applies to the (ac) plane] and t_{sp2} [which applies to the c positions in the (ab) plane] so that it is not possible to identify reliably any crystal axis which is significantly more difficult for the l vector than the other axes. In particular, the effective anisotropy field in the (ac) plane near T_N (which can be estimated from the spin reorientation field measured by Voigt[21]) amounts to $H_A\approx 1$ kOe and the corresponding estimate $t_{co}\approx 3\times 10^{-3}$ for the $(2\to 1)$ transition lies close to the lower limit of the region where β was determined.

In our opinion, iron orthoborate is more likely to exhibit planar than Ising behavior in the interval $2\times 10^{-3}<t<8\times 10^{-2}$, although its index β is somewhat less than for the other members of this class of materials because of the proximity of $t_{co}(2\to 1)$ to the limit of the range where the measurements were carried out. Therefore, a theoretical model with scalar order parameters proposed by Sokolov[20] to explain the splitting of the critical exponents of the Fe_3BO_6 sublattices can hardly be applied to this material in the range $t>10^{-3}$. Therefore, it would be interesting to search for many-sublattice compounds characterized by a strong axial anisotropy $[t_{co}(3\to 1)\approx 10^{-1}]$ which may exhibit splitting of the critical exponents in the temperature range $10^{-3}<t<10^{-1}$ in accordance with the predictions of Sokolov.[20]

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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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