Chapter 5

Resonance properties of low-temperature magneto-dielectrics under hydrostatic pressure

The radio-frequency and microwave microscopy methods make it possible to obtain information on interrelation between electronic states and positions of atoms and ions in the structure of a solid. Being sensitive to any changes of the structure, the resonance methods combined with hydrostatic pressure evoking changes of the structure parameters are effective ways of investigations of complex processes in the vicinity of structural phase transitions [106-109].

The design and creation of high-pressure and resonance techniques relates largely to the parameters of loading, resonance conditions and the degree of compressibility of a sample.

Rich bibliography on the high-pressure technology and resonance and magnetic investigations can be found in [110-112] showing the level of achievements in this field. The analysis of the results of the studies of phase transitions by resonance methods under pressure has shown that they contribute a lot to changes of the properties of ferroelectrics and ferromagnets [113]. The relationship between the magnetic properties and changes of the lattice parameters shown by the example of compressibility for MnF_2 and Cr_2O_3 as well as the numerical value of $dT/dP = 1.6\ cal/kbar$ tell about the second-order PT indicated by negative changes of the critical temperature under pressure [114-116].

The shift of the resonance frequency modes F_0^{2x} MnO, MNF_2 under hydrostatic pressure makes it possible to specify features of the structural phase transition [117]. The pressure realizes transformations of the structure, the dynamics of the phase states that is accounted for, in model representations through the renormalization of the constants [118]. The authors of [119] have theoretically shown the dynamics of changes of the resonance properties during the formation of the structural phase transition. The analysis of the data on $CuCl_2 \cdot 2H_2O$ NMR studies under pressure was the basis for the high-frequency branch calculation with the pressure parameter taken into consideration [120]. For the low-frequency spectrum [6], the region of the field-temperature dependence was shown in the form of resonance absorption both in the phase state and in the region of the first-order structural phase transition in the easy and hard planes.

By determining the thermodynamic state of a solid through relationship of the temperature and the volume, we can place the dependence of the temperature change in correspondence with the structural changes of the volume and the properties, consequently. There occurs a transformation process: first we deal with one type of the energy which is the heat transformed into the energy of elastic stresses deforming the structure and changing the properties. A similar process of elastic changes of the structure results from the hydrostatic pressure effect.

The studies of regularities and phenomena in the physical process of structure changes in the low-temperature range and under the influence of magnetic field and high hydrostatic pressure together with the resonance registration procedure for objects of good compressibility enable us to determine the interactions under the formation of phase transitions and to compare the effects of pressure, temperature and magnetic field. The hydrostatic pressure effect conforms to the effect of thermoelastic and magnetoelastic compression. In the physics of magnetic phenomena, there are not so many papers dealing with the investigation of high-density samples at variable temperature and magnetic field and under pressure effect. In this case, the efficiency of high hydrostatic pressure action on the structure parameters and as a consequence on the magnetic properties on magnet-containing media is obvious but insignificant. For such investigations, the most promising are model single crystals of good compressibility. These are magnetodielectrics $CuCl_2 \cdot 2H_2O$ and its isotopic analogue $CuCl_2 \cdot 2D_2O$.

5.1. Resonance properties and pressures in inclined magnetic fields

The sensitivity of the resonance properties to the hydrostatic pressure observed during complex investigations of the low-frequency branch has shown dynamic changes of the phase state prior to PT as well as the dependence of the region of first-order structural phase transition realization on the mechanisms of elastic stresses. The investigations were done at frequencies of the decimeter range in a broad pressure range to 10kbar. The preliminary result [18, 102] has shown that for 3.7 GHz and 0.9 GHz, the resonance absorption lines for a higher H, pressure increase and a fixed temperature, coincide in the whole pressure range (Fig. 5.1). The changes of the form of a dip observed at small angles and low temperatures disappear with the pressure and the temperature increase.

More detailed investigations were done for a minimal temperature of 1.68 K at frequencies of 2.85-3.15 GHz, 4.5-4.8 GHz and 0.75-0.63 GHz under the fixed pressures of 5.2, 9.2, 11.2 kbar (Fig. 5.2, 5.3).

The external magnetic field H was oriented in the ab-plane and varied to within 6.2 kOe (Fig. 5.3). In this case, the resonance absorption lines belonged tone and the same field for all the frequencies and fixed pressures. There were no changes of the character of the low-frequency branch. For H to a-axis, the resonance fields were displaced thus pointing to the first-order structural phase transition.

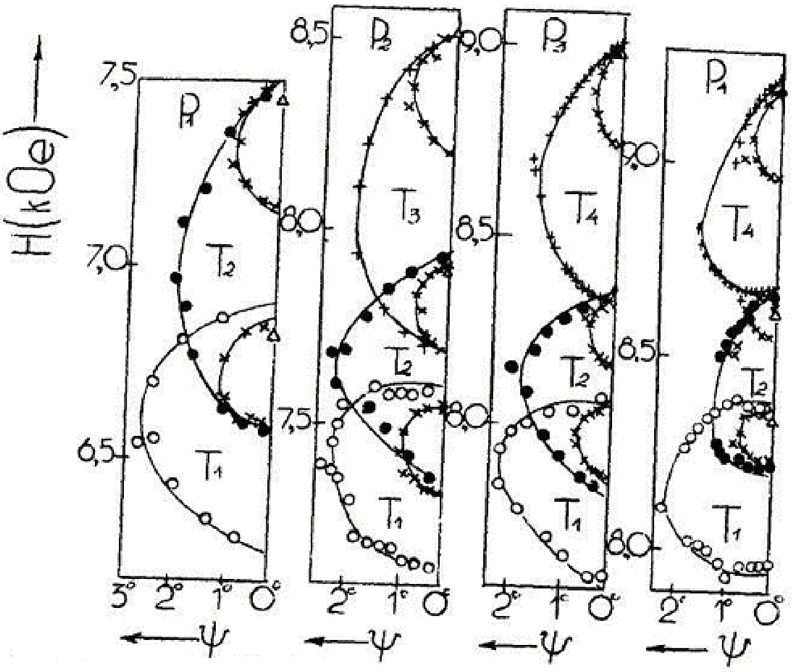

Figure 5.1. The dependence of the fields of resonance absorption on the deviation of the magnetic field at easy plane and fixed temperatures and pressures in $CuCl_2 \cdot 2H_2O$: T_1=2 K, T_2=3 K, T_3=4 K, T_4=4.2 K; P_1=0, P_2=5.2 kbar, P_3=9.2 kbar, P_4=11.2 kbar; $\omega_1(\Delta)$=0.76 GHz, $\omega_2(\times)$=3.14 GHz, $\omega_3(\circ)$=4.88 GHz [18].

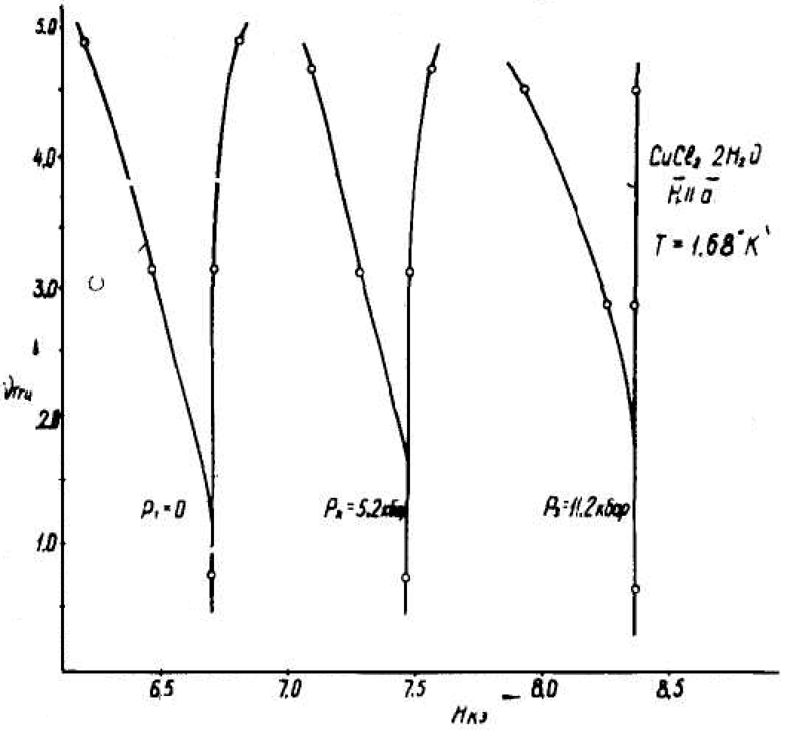

Figure 5.2. Frequency-field dependence of the fields at fixed pressures P_1=0, P_2=5.2 kbar, P_3=11.2 kbar and T=1.68 K.

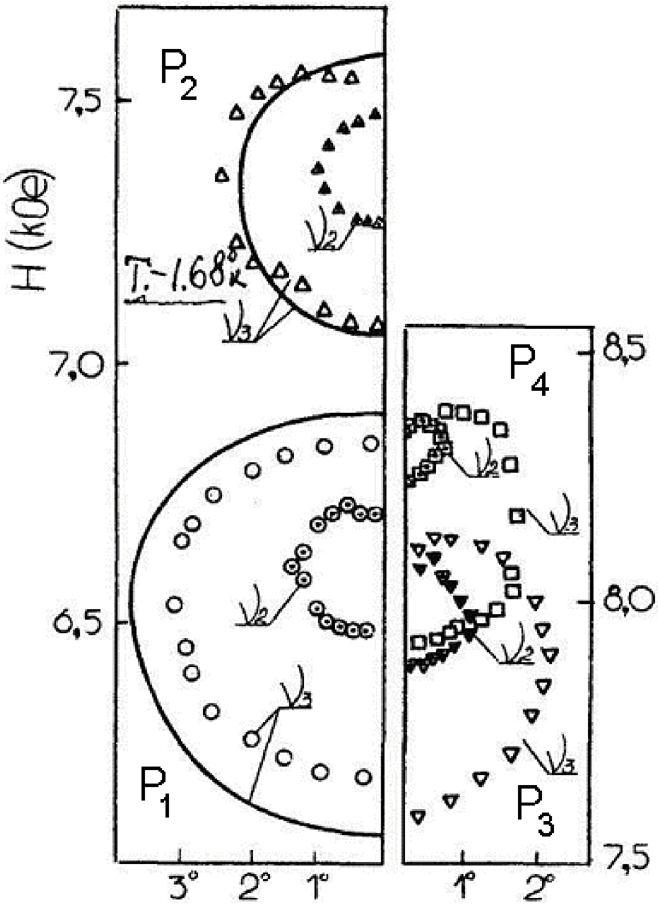

Figure 5.3. The fields of the resonance at H deviation on the easy plane at $P_1=0$, $P_2=5.2$ kbar, $P_3=9.2$ kbar, $P_4=11.2$ kbar and $\omega_1=2.85$ GHz, $\omega_2=4.88$ GHz at T=1.68 K [18].

From the analysis of the experimental data on the position of H field, the resonance in the PT region for different pressures and temperatures, it follows that with hydrostatic pressure increase, the conditions for structural phase transition realization are equivalent to the temperature decrease by their effect.

Another case relates to studying the conditions of resonance absorption with the fixed temperature growing from 1.68 up to 4.2 K. The magnetic field was oriented in ab-plane. For $T\neq0$, the region of stable resonance observation propagated to the maximum of 3K. And the position of low-frequency section of the field-temperature dependence was unchanged. With the pressure increase, the boundaries of stable resonance observation reached 4.2 K. The broadened temperature range is shown on the field-temperature dependences which are shifted to higher fields with angular diagram change. Characterizing the nature of the observed phenomena in all the investigations, we note changes in H-resonance in the region of the structural phase transition while the dynamics of the changes corresponds to the first-order phase transition. A lower resonance field belongs to the phase state discussed in [6]. In view of the results of [64], it is concluded that the resonance absorption branch covers the region of PT formation on the whole of the low-frequency branch (up to the frequency of 4.62 GHz). With the pressure increase, the region changes very much, making it possible to relate the uniform compression to the energy of structural interactions that provide perfect information on the dynamics of the first-order structural phase transition in a magnet-containing media. So, the constants $\lambda = 44\,kbar^{-1}$, $\lambda = 2\,kbar^{-1}$, $\lambda = 0.14\,kbar^{-1}$ have been evaluated enabling the binding of energies to restore the curves of the phase states.

5.2. Resonance and pressure in magnetodielectric $CuCl_2{\cdot}2D_2O$

The investigations of single crystals distinguishable by minor structure changes and prepared by X-ray methods and H_2O substantiation for D_2O resulting in changes of the distance between the lattice sites. This substantiation results in negligible stretching of the lattice along b- and c-axes. The low-frequency branch of the resonance absorption was studied in $CuCl_2{\cdot}2D_2O$ at the frequencies $\nu_1 = 0.832\,GHz$, $\nu_2 = 2.206\,GHz$ and $\nu_3 = 4.531\,GHz$ in 1.74-4.2 K temperature range and under pressures between 0-7 kbar. In H field of the easy magnetization of a-axis and at T=1.74 K (Fig. 5.4), the field-temperature dependence resembles the dependence for $CuCl_2{\cdot}2H_2O$ [65]. The curves for $CuCl_2{\cdot}2D_2O$ are 80-100 Oe displaced to lower fields. The type of the dependences

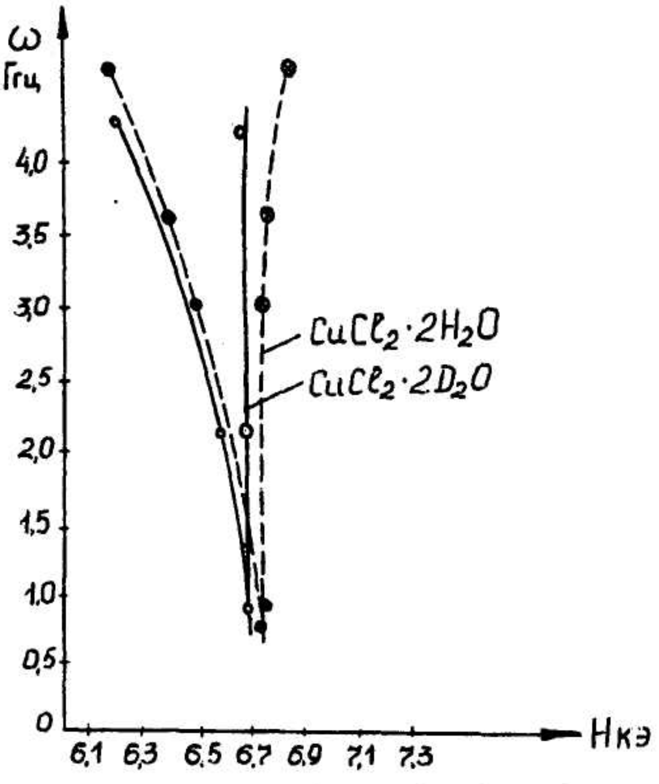

Figure 5.4. Frequency-field dependence for $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$ at T=1.74 K [122].

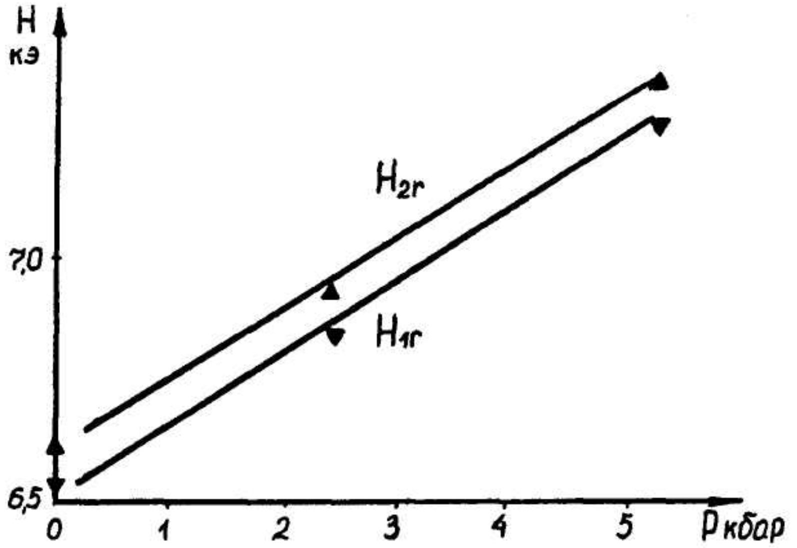

Figure 5.5. The pressure dependence of the resonance fields in $CuCl_2{\cdot}2D_2O$.

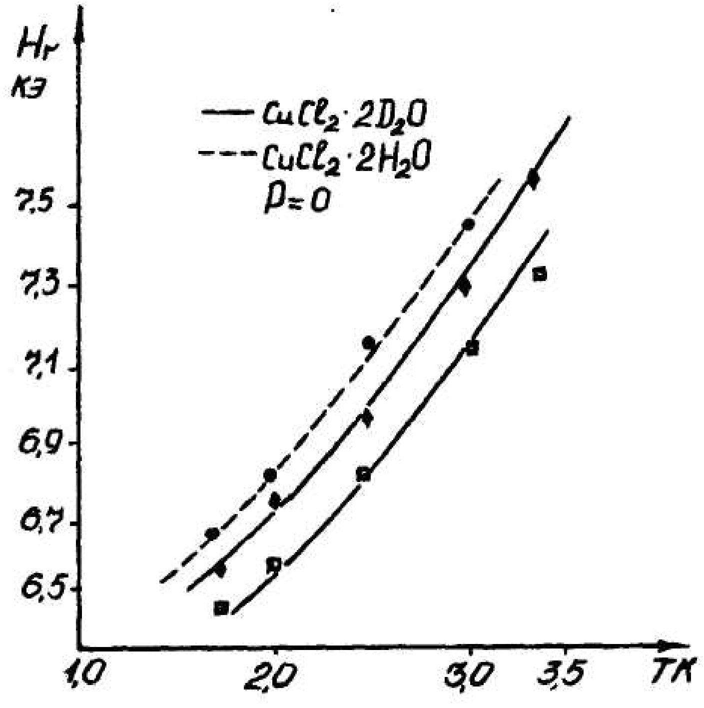

Figure 5.6. The resonance fields of PT in $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$.

remains unchanged pointing to the invariant character of the first-order structural phase transition and the resonance absorption in both the phase state and the region of the phase transition [121]. The phase transition character retains with the introduction of the hydrostatic pressure parameter [122]. The dependence of Fig. 5.5 shows a linear growth of the resonance absorption fields in the area of PT with the derivatives with respect to the pressure $\lambda = 0.143\, kOe \cdot kbar^{-1}$

and $\lambda = 0.14\,kOe \cdot kbar^{-1}$, respectively. The discrepancy of the parameters is a consequence of the changes of the parameters and the decrease of binding energies and stresses.

The temperature dependences of the resonance absorption fields are lower than those for $CuCl_2 \cdot 2H_2O$ for all the pressures and repeat the regularities of the changes in PT region. There are also differences in the values of the resonance fields of 100-200 Oe (Fig.5.6 of the preprint) [65, 122].

The temperature dependence of the field of the structural phase transition can be written as [120, 123]:

$$H(T) = H_0 + xm^2 \text{ , where } H_0 = 65\,kOe \text{ and } L = 0.07\,kOek^{-2}$$

This expression describes the character of temperature changes in the field of the first-order structure phase transition in a qualitatively correct way. For $CuCl_2 \cdot 2D_2O$, L parameter is equal to 0.0803 $kOe \cdot cal^{-2}$ and it is somewhat different from the analogue. For T=0 K, H_0=6.38 kOe. The investigation of the temperature dependence of resonance fields for different pressures [122] changes similarly for $CuCl_2 \cdot 2D_2O$ and its analogue, i.e. there is a decrease in dH/dP gradient value.

Dependence of resonance fields upon the displacement of the external magnetic field. The regularities are repeated in the whole the temperature range (1.74-4.2 K) and for the pressures to 5.3 kbar as well as in the dynamics of stall-angle behavior. The angles are decreasing with pressure.

5.3. Dynamics of width and intensities of resonance absorption lines under pressure and temperature

For a more complete study of the changes of the character of phase states we consider the dependencies of intensities and width of resonance absorption lines in the low-frequency region.

With the magnetic field H oriented strictly along the easy magnetization axis a, the line corresponding to the absorption in the phase state is an order of magnitude intensive with respect to the line that fixes the region of the phase transition. Under magnetic field deviation by the angle of 0.3°, the intensities relate as 2 to1, respectively, they coincide in the region of stall angles (Fig. 5.7). This behavior was regular for all the studied frequencies.

The resonance fields were studied simultaneously with the half-width of resonance absorption lines [122]. With H || to the easy magnetization axis a, for T=1.74-3, the half-width did not exceed 20 Oe (Fig. 5.8). For the pressure of 0,53 GPa, the temperature range increases to 4.2 K and till 2.5 K the widths decrease to10 Oe and are increasing to 50 Oe at 4.2 K (Fig. 5.9).

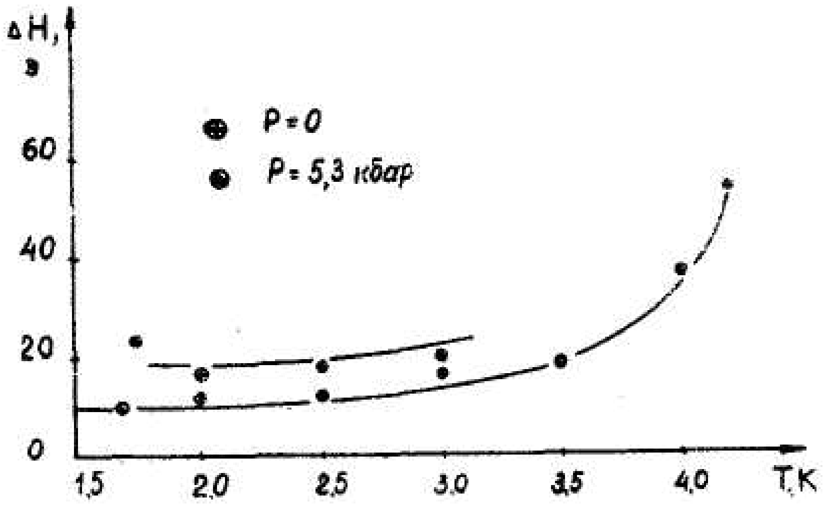

Figure 5.7. Temperature-field dependence of the width of the resonance fields in $CuCl_2 \cdot 2D_2O$ at the fixed pressures $P_1=0$ and $P_2=5.3$ kbar; ω=0.806 GHz [122].

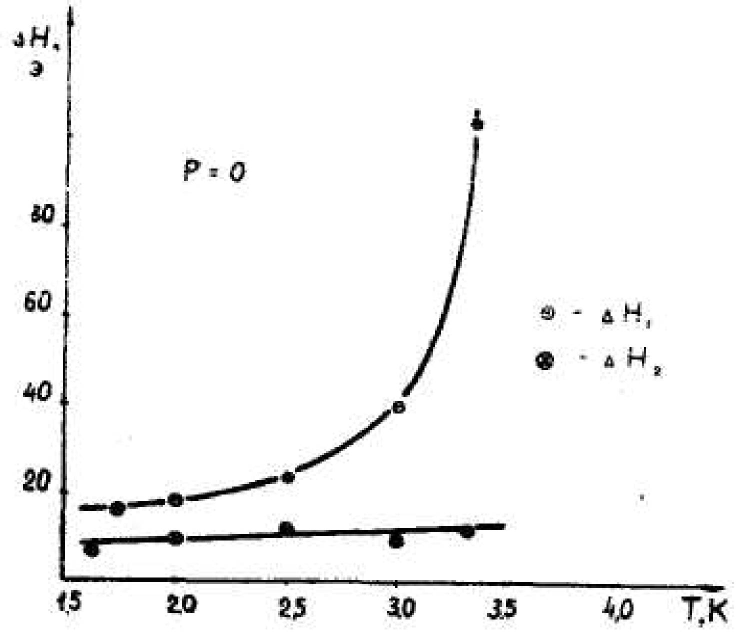

Figure 5.8. The temperature dependence of the resonance width at P=0; ω=2.206 GHz [122].

It follows that there is the essential difference in the dynamics of the behavior of the resonance absorption like half-width in the phase state and in the area of the phase transition. The half-width of the resonance absorption corresponding to the phase state field does not practically depend on the temperature and is insignificantly influenced by the frequency and the pressure. In the area of the structural phase transition, the resonance absorption half-width considerably varies with the temperature and toa less degree with the pressure increase.

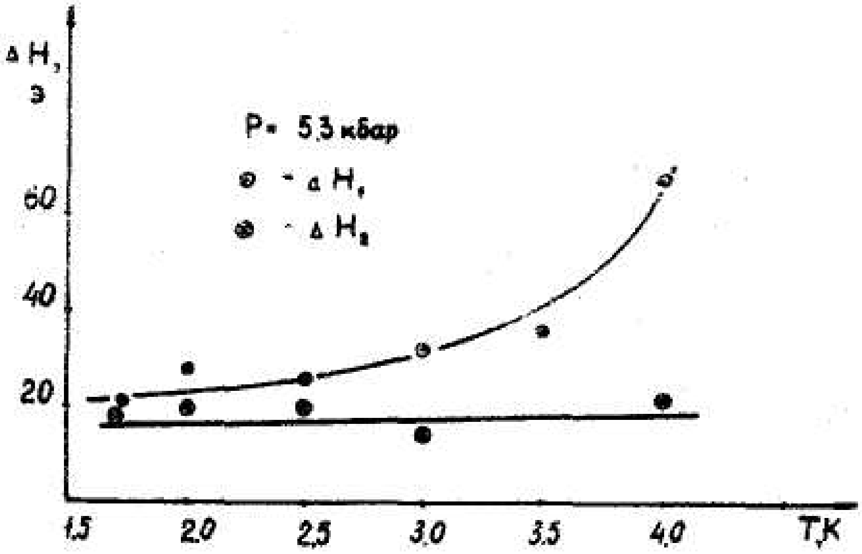

Figure 5.9. The temperature dependence of the resonance width at P=5.3 kbar; ω=2.206 GHz.

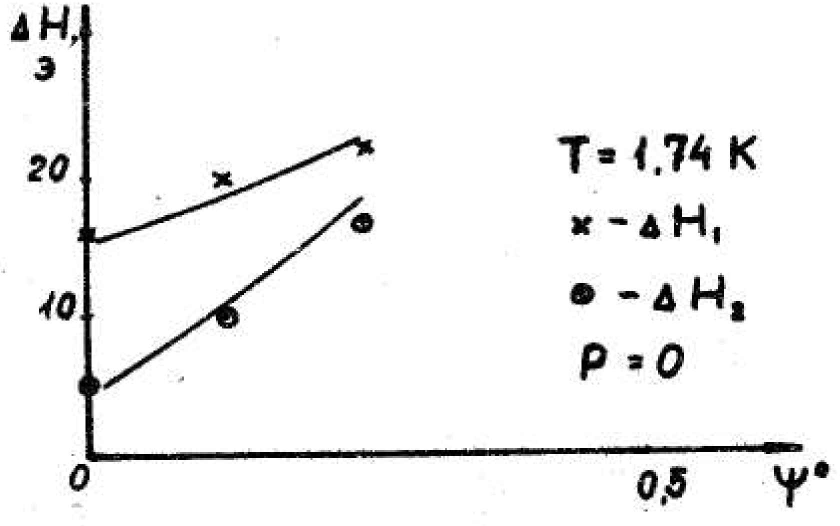

Figure 5.10. The dependence of the width of resonance absorption at the deviation of the magnetic field on the easy plane at T=1.74 K; ω=2.206 GHz.

It should be noted that the growth of the hydrostatic pressure changes parameters of the structure at the expense of compression, redistributes the relationship between the binding energies and elastic stresses and influences the electron mobility. For a more detailed analysis, an additional set of the experimental results is required. However, even this result differs very much from analogous investigations done at other frequencies [124] where the width of ~5Oe and lower were obtained due to a special processing of the samples. It is difficult to compare the results of [125] because there are practically no calculations done for low-temperature magnetodielectrics studied, as a rule, for T lower than the critical one.

The measurements made on the studied dielectrics show that there exist regularities in the changes of the half-width of the resonance absorption lines when the magnetic field H deviates from the easy magnetization axis a. The results demonstrate that at low temperature, minor changes in the area of the phase transition correspond to 20 Oe and the same is observed with the temperature increase (Fig. 5.10). The region of the phase state fixed by H varies within 90-120 Oe with the temperature growth and under a 0.5° deviation of the field from a-axis (Fig. 5.11). In this case and in the mentioned conditions, the resonance line widths are little influenced by the pressure (Fig. 5.12).

By comparing the results of $CuCl_2{\cdot}2H_2O$ and its isotopic analogue investigations, we can note the identical dynamics of changes of the properties in the area of the first-order structural phase transition as well as some difference in lattice parameters along b and c-axes. As a result, there is a difference in phase diagrams and a 100-120 Oe difference in the fields. The character of the first-order phase transition was unchanged for all ranges of frequency, temperature and pressure.

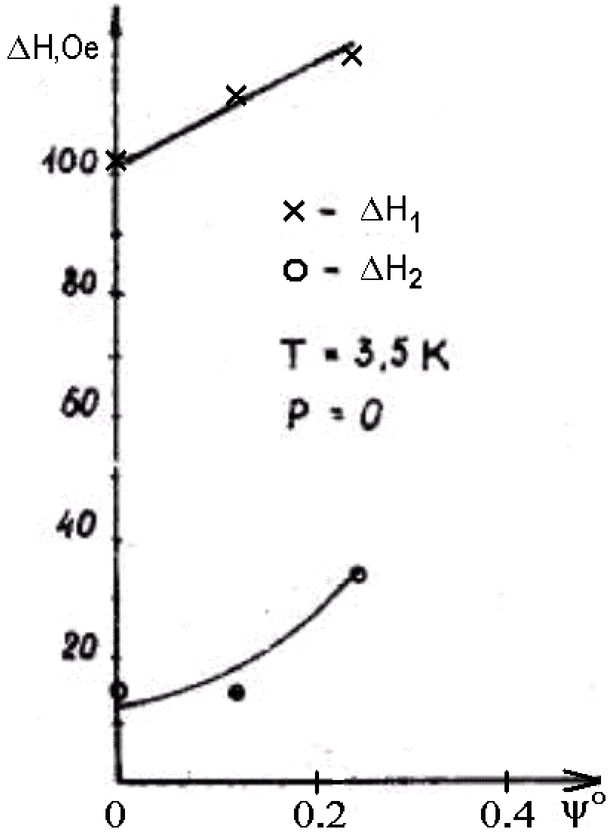

Figure 5.11. The dependence of the width of the resonance absorption at the deviation of the magnetic field on the easy plane at T=3.5 K; ω=2.206 GHz.

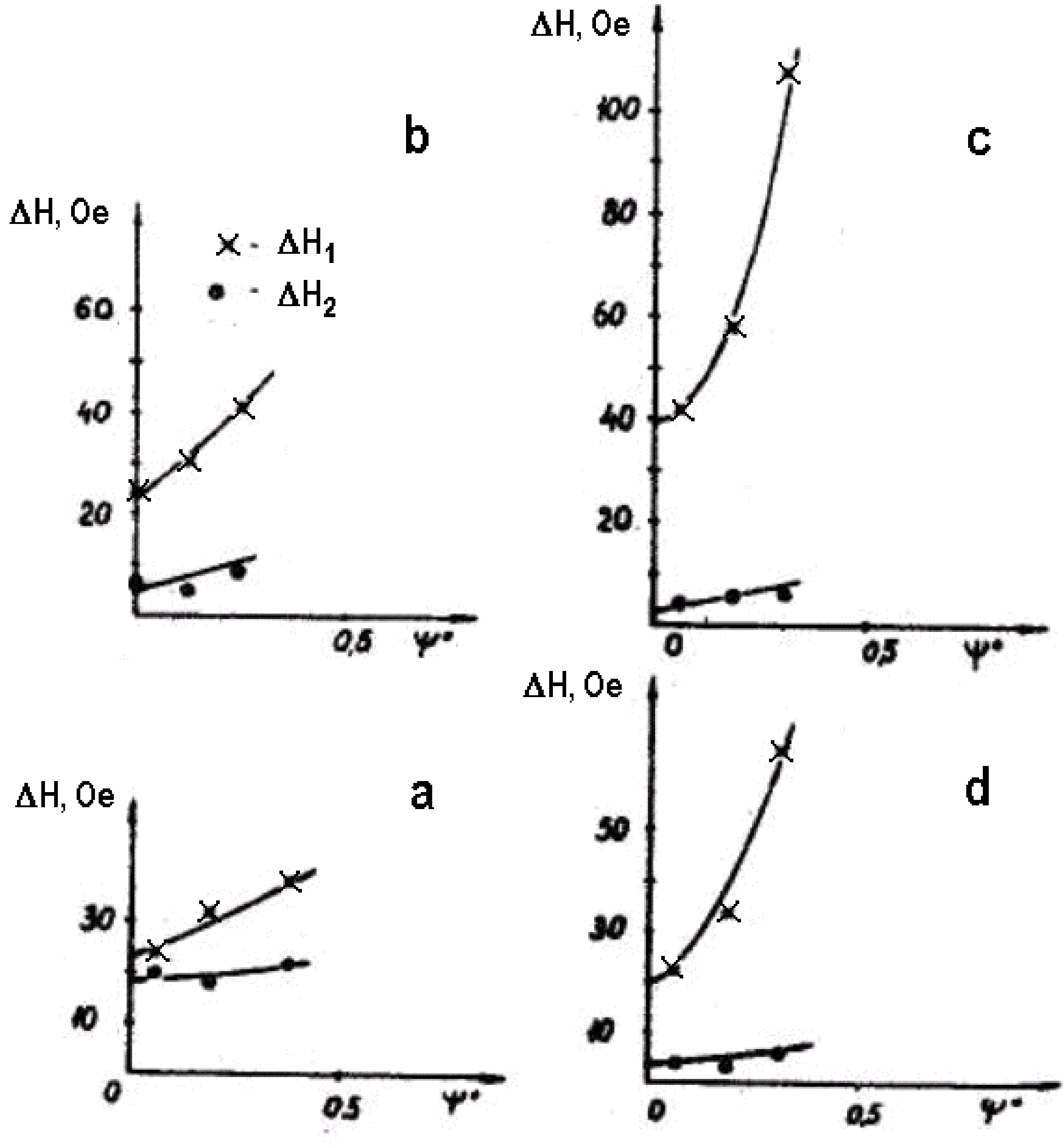

Figure 5.12. The dependence of the width of the resonance absorption at the deviation of the magnetic field on the easy plane at the fixed pressure P=5.3 kbar and the temperatures: a) T_1=2.5 K, b) T_2=3 K, c) T_3=3.5 K, d) T_4=4 K.

5.4. Conclusions

The resonance methods are sensitive to any changes of the crystal structure influenced by elastic stresses. Thus, it is possible to investigate complex processes developing in the neighborhood of structural phase transitions and phase states under T-H effect and uniform compression by hydrostatic pressure P. The meaningful dependence of the parameters of hydrogenated single crystal and good compressibility make it possible to distinguish experimentally the parameters of bonds and interactions that correlate with interatomic distances. The results of investigations explaining how the pressure affects the resonance properties in the region of the phase states and structural phase transition establish the regularities for the critical points and the lines separating the phase states as well as for the resonance spectrum.

The represented dependences give us regularities of the resonance absorption showing that the increase of the pressure broadens the temperature range of resonance observation that is shifted to higher fields. On the dependence of the resonance fields, the depth of the dip increases near the distinguished easy axis. In the considered phases, the difference between the fields becomes smaller, the temperature range with stable resonance field fixation becomes broader and the PT critical line is shifted to higher fields.

It follows that the hydrostatic pressure increases the resonance fields and demonstrates the role of elastic stresses in the considerable change of interatomic distances with fixed T and H. As far as the nature of the upper resonance field correlates with the region of the first-order structural phase transition and the pressure from the uniform compression influences the anisotropy of interatomic and structural interactions, the dynamics of their changes gives us the information on PT state in magnet-containing medium within the low-temperature region. As a result, it has become possible to estimate the magnetoelastic constants.