CHAPTER 3

Elastic and structural properties of hydrate-containing ferrites

Phase diagrams of ferrites with evident uniaxial anisotropy have been studied for a long time in the course of physics of magnetic phenomena [36-39].

By the mid-60ies, experimental and theoretical investigations were done, in which the idea of anisotropy presence in two planes was developed and elaborated on [39]. These studies resulted in fixing the plane where the phase transformation is formed. The investigation of $CuCl_2{\cdot}2H_2O$ [40-42] have shown that there is a phase transition on the phase diagram in inclined magnetic field below T~4.2 K. The phase diagram undergoes strong changes if the field is varied near the anisotropy axes [43]. There exist values of angles where magnetic properties are changed too, i.e. the phase transition disappears. Identical samples of $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$ were taken for the analysis. They were the crystals of low-temperature ferrites of the same symmetry group D_{2h}^7- P_{emn} without axes higher of the second order of symmetry. The analysis of structural and magnetic properties obtained by different methods gave us a possibility of both qualitative and quantitative control of the validity of our results.

The crystal structure of $CuCl_2{\cdot}2H_2O$ (Fig. 3.1) was considered in detail in [45-50]. The crystal had three binary axes and three planes of symmetry. The structure of $CuCl_2{\cdot}2D_2O$ was investigated in [44, 45, 51]. The values of the parameters are listed in Table 3.1. The crystalline field of approximately rhombic symmetry was acting on copper ions in $CuCl_2{\cdot}2D_2O$.

In $CuCl_2{\cdot}2H_2O$, the magnetic ordering determined by NMR method [45, 49] had shown that magnetic moments of copper ions lying in (ab) plane were ordered ferrimagnetically. The period of the magnetic unit cell 2x3.7 Å was twice larger of the crystal-chemical cell, the direction of the easiest magnetization was aligned with $\overline{a}$ axis. In the single crystal, the magnetic ordering was directly observed by magnetic neutron diffraction analysis at T=1.5 K [52, 53]. A model was proposed [26] where the local environment of the magnetic ion assumes non-zero anti-symmetric super-exchange interactions. Typical bevel of the spin moments in $\overline{ac}$ and $\overline{ab}$ planes is taken into account by renormalization of the fields of magnetic anisotropy in relativistic branches. The data of neutron diffraction [54] give the value of 0.353 K characterizing the bevel of spin moments in $\overline{ac}$ plane.

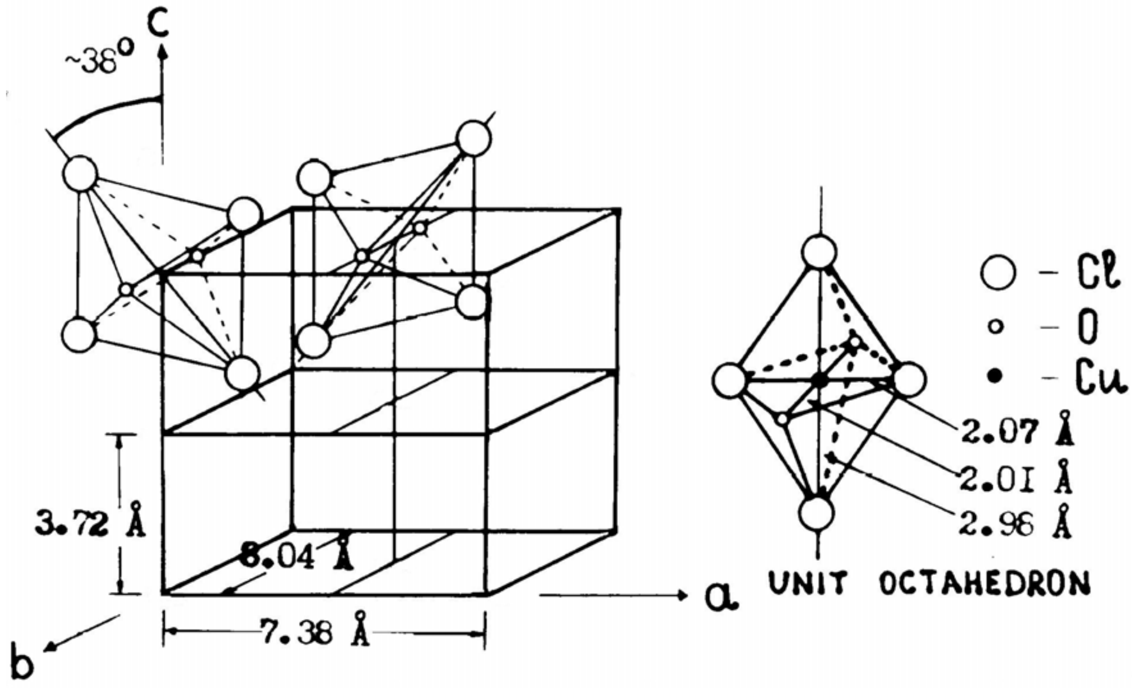

Figure 3.1. The crystal structure of $CuCl_2{\cdot}2H_2O$.

Table 3.1. The results of X-ray investigations.

	$CuCl_2{\cdot}2H_2O$		$CuCl_2{\cdot}2D_2O$	
	Data of [23]	Measurements	Data of [19]	Measurements
a	7.41(2) Å	7.436±0.003 Å	7.38 Å	7.436±0.003 Å
b	8.08(2) Å	8.148±0.001 Å	8.04 Å	8.027±0.001 Å
c	3.74(1) Å	3.756±0.006 Å	3.72 Å	3.751±0.006 Å
K_a		$(2.39\pm0.07)\cdot10^{-12}$ cm^2/dyn		$(2.49\pm0.07)\cdot10^{-12}$ cm^2/dyn
K_b		$(0.95\pm0.06)\cdot10^{-12}$ cm^2/dyn		$(1.02\pm0.06)\cdot10^{-12}$ cm^2/dyn
K_c		$(2.40\pm0.07)\cdot10^{-12}$ cm^2/dyn		$(2.53\pm0.07)\cdot10^{-12}$ cm^2/dyn
χ		$5.74\ 10^{-12}$ cm^2/dyn		$6.03\cdot10^{-12}$ cm^2/dyn

Both the neutron diffraction analysis and the spin – echo method [55] assume the existence of the structure of four sublattices splayed from $\bar{a}$ axis to $\bar{c}$ axis. The analysis of this model [54, 56] has shown that the bevel of magnetic spins in $\overline{ac}$ plane is possible but it is practically vanished in $\overline{ab}$ plane. In these systems, a weak ferromagnetism can develop according to the symmetry discussed in [57]. It can be accounted for by renormalizing of the number of constants of exchange and relativistic anisotropy in the first and the second approximations. The resonance properties are not affected in areas of low frequencies and low fields and so, they are not the subjects of investigations in the low-frequency range.

Unfortunately, an attempt of revealing of weak ferromagnetism [44, 51] by neutron diffraction methods did not give a convincing result for $CuCl_2{\cdot}2D_2O$.

The studies of magnetization in the magnetic field in a wide temperature range by Faraday method [40] have resulted in a statement the in the paramagnetic region the susceptibility obeys Curie-Weiss law

$$\chi = \frac{\delta}{H} = \frac{c}{T-\theta} \quad \theta \simeq 5K$$

and for T=4.23, K M(T) dependence has a typical jump corresponding to a phase transition. For T=4.3 K, a jump in the heat capacity is accompanied by an anomaly.

While observe the character of changes of magnetization along three axes at T lower than 4.3 K, the authors of [40] stated that magnetization is of several hundreds Oe along $\overline{a}$ axis till H=6.5 kOe, then it increases rapidly and becomes proportional to the field in strong magnetic fields. The general pattern of magnetization in $\overline{ac}$ plane is similar to the behavior in $\overline{ab}$ plane for T<T. However, the comparison of $\delta = f(H)$ of both the planes shows that $\chi_a = 1.702 \cdot 10^{-4}$, $\chi_b = 1.48 \cdot 10^{-4}$, $\chi_c = 1.83 \cdot 10^{-4}$ at $\chi_b < \chi_a < \chi_c$. One of the most popular methods is the study of magnetization in the pulse field that enables the estimation of He exchange field and anisotropy field on the mentioned axis. Thus, $H_e = 7.4 \cdot 10^4\, Oe$, $H_A = 3.3 \cdot 10^2\, Oe$ [58] differ very much from $H=1.5{\cdot}10^5$ Oe [59].

Studies of magnetization in $CuCl_2{\cdot}2H_2O$ [60] gave the following values of the fields: $150 \pm 2\,kOe$, $161 \pm 2\,kOe$, $146 \pm 2\,kOe$ directed along $\overline{a}, \overline{b}, \overline{c}$ axis, respectively. The values of interaction between layers of ferromagnetic ordering of copper ions lying in the plane aligned with $\overline{c}$ axis were found to be $y = 5.51 \pm 0.07K$ and $y = 0.67 \pm 0.08\,K$ in $\overline{(ab)}$ plane.

The temperature of PT depended on the direction of applied magnetic field.

The temperature dependence of the field of phase transition was analyzed by the jump of heat capacity [62]. The method of nuclear magnetic resonance is the most informative one. It was used for the study of regularities of the first-order PT [63, 64] in $CuCl_2{\cdot}2H_2O$ where changes of Hp as a function of temperature and inclination to the easy axis were observed. The method enables us to analyze the phase diagram (HT) to determine parameters for the existence of PT at ~150 Oe and to evaluate the critical region of phase transition $\psi_c \sim 11'$ for T=1.84K.

The changes of magnetization of a ferrite in the magnetic field result in deformation thereof (the magnetostriction is involved). The magnetostriction phenomenon relates to processes and interactions in the structure. The changes of the energy of interaction in view of deformation can be accounted for by additional magnetoelastic and elastic components introduced to free-energy density of magnet-containing crystals. The “free-energy” term implies a great number of phenomenological constants characterizing the magnetic, magnetoelastic and elastic energy. The parameters can be determined experimentally with arbitrary stress-tensor components, and by measurement of variable strains and components of vectors $\vec{l}$, $\vec{m}$. This data set would help in the determining and the control of experimental results and theoretical statements. We consider hydrostatic pressure as a convenient external parameter affecting properties of the sample, temperature changes of PT, frequencies of the critical-point resonance. So, we can determine combinations of magnetostriction constants by virtue of pressure-dependent parameters.

For single-crystalline hydrate-containing samples, the compressibility is one of important parameters. The changes of the interplanar spacings, determination of coefficients of anisotropy of compressibility for the principal crystallographic directions give us complete information about relative changes of lattice parameters which are an important factor for PT and ferrite properties.

3.1. Structural peculiarities and determination of compressibility parameters for hydrate-containing single crystals

Studies of $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$ structures gave almost identical parameters [48, 50] that pointed to X-ray diffraction analysis application for testing.

X-ray diffractometer of DRON-1.5 type was used for estimation of coefficients of compressibility along principal crystallographic directions. The measurements were made at room temperature. The high-pressure chamber [34] was used. The chamber design made it possible to make measurements by X-ray diffractometer with scanning under pressure without the chamber removal from the goniometer. These arrangements excluded measurement errors because of multiple dismounting of the chamber from X-ray device, thus the accuracy was a increased. The pressure-transmitting medium was petrol. The pressure was varied within 0÷0,2 GPa and measured by a pressure pick-up.

The compressibility was determined during the investigations of interplanar spacings along (400), (040) and (003) directions. X-ray photography was conducted in cobalt radiation. Fig. 3.1 illustrates experimental values of the intercrystalline spacings d_{400}, d_{040}, d_{003} in the 0÷0,2 GPa pressure range. Experimental points were processed by the least-square method with linear dependence taken into account. The results of the processing are solid lines (see Fig. 3.2). For the maximum accuracy of relative interplanar distance measurements in the course of pressure change, the profiles of diffraction lines were recorded automatically and fixed in the constant range of angles with X-ray tube and quantum counter operating continuously. The total experimental error consisting of the error of determining of lattice parameters and pressure error did not exceed 3%.

The coefficients of compressibility K_a, K_b, K_c along the corresponding crystallographic axis calculated for the orthorhombic structure of the investigated crystal are as follows:

$K_a=2.49\cdot10^{-12}$ cm^2/dyn,
$K_b=1.02\cdot10^{-12}$ cm^2/dyn,
$K_c=2.52\cdot10^{-12}$ cm^2/dyn.
The total compressibility $K=6.03\cdot10^{-12}$ cm^2/dyn.

As noted above, the experimental points were processed by the least-squares method with the linear dependence taken into account. The X-ray photography was made in cobalt radiation. The results are listed in Table 3.1. For comparison, there are crystal lattice parameters obtained by other authors. As for the compressibility, such studies have not been done beforehand, as we know.

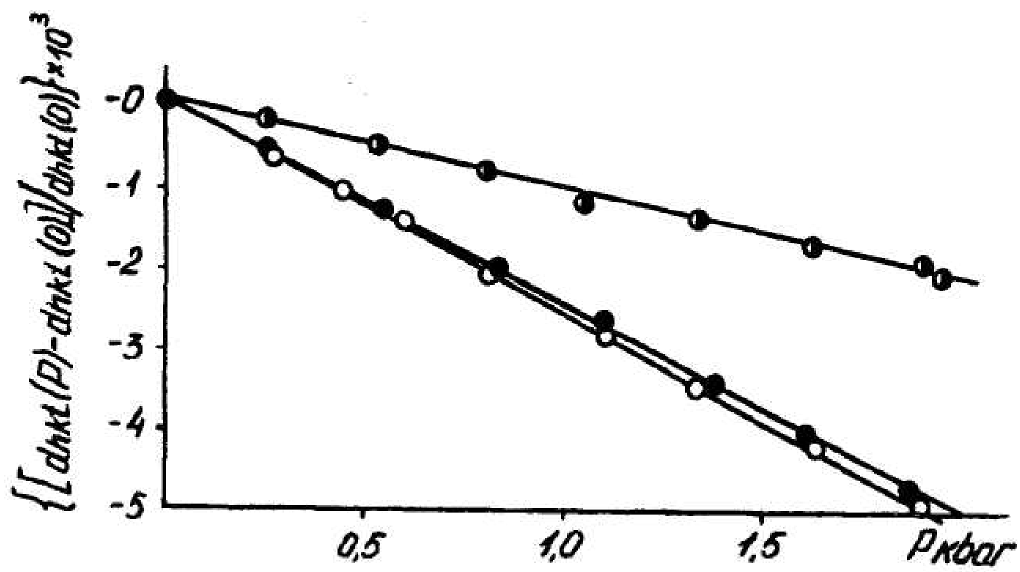

Figure 3.2. Dependence of interplanar spacings d_{400}, d_{040}, d_{003} on uniform compression in $CuCl_2\cdot2H_2O$ [64, 65].

Analogous experiments were done with $CuCl_2{\cdot}2D_2O$ [53]. In this case, the X-ray photography was done in copper radiation. The interplanar distances d_{800}, d_{010}, d_{003} were determined. The coefficient of compressibility were derived from pressure dependencies of interplanar distances d_{400}, d_{040} and d_{003} similar to $CuCl_2{\cdot}2H_2O$.

The data on compressibility for $CuCl_2{\cdot}2D_2O$ are listed in Table 3.1.

The testing of $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$ is in a good conformity with the data obtained from other experiments. The results point to the difference of copper chloride dehydrate parameters from those of $CuCl_2{\cdot}2D_2O$ along $\bar{b}$ and $\bar{c}$ axis as well as to divergences in linear and bulk compressibility.

3.2. EPR investigations in $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$ under pressure

In a broader temperature range, where AFMR frequencies could be observed under pressure, T_N was shifted toward higher temperatures.

To study this regularity, the EPR method was proposed. More exactly, it was EPR vanishing at the boundary of the transition [64]. The EPR lines broaden abruptly near T=4.5 K when Neel temperature is approached and practically disappear at $T-T_N=0.01$ K. $T_N(P)$ dependences give values of Neel temperature derivative with respect to pressure $dT_N/dp = 0.185\,K \cdot kbar^{-1}$. In the experimental study of EPR under pressure [64], the external magnetic field was oriented strictly along $\bar{a}$ axis. With the value of the field under which EPR was observed and the frequency, the value of g-factor for $CuCl_2{\cdot}2H_2O$ can be derived from the relation

$$h\nu = q\mu_B H \tag{3.1}$$

where h is Dirac action constant, ν is the frequency, q is the factor, μ_B is Bohr magneton, H is the value of the external field.

For P=0, the frequency was ν=4.539 GHz, the field where EPR was observed was H=1.493 kOe. Thus, q-factor was evaluated as 2.173.

For P=3.1 kbar, the frequency ν=4.72 GHz, the corresponding field was 1.57 kOe. In this case, q=2.149. We note a good agreement between the obtained q-factor value for zero pressure and those from [66-68].

However, the data for dT_p/dp obtained by NMR method [50, 71] somewhat differ from the present data. We have dT_p/dp =0.18 $K{\cdot}kbar^{-1}$. This difference can be due to, first, different accuracy of pressure measurements, second, the difference in registration of the temperature by the both methods. Third, NMR measurements are made at higher values of external magnetic field as compared to EPR method.

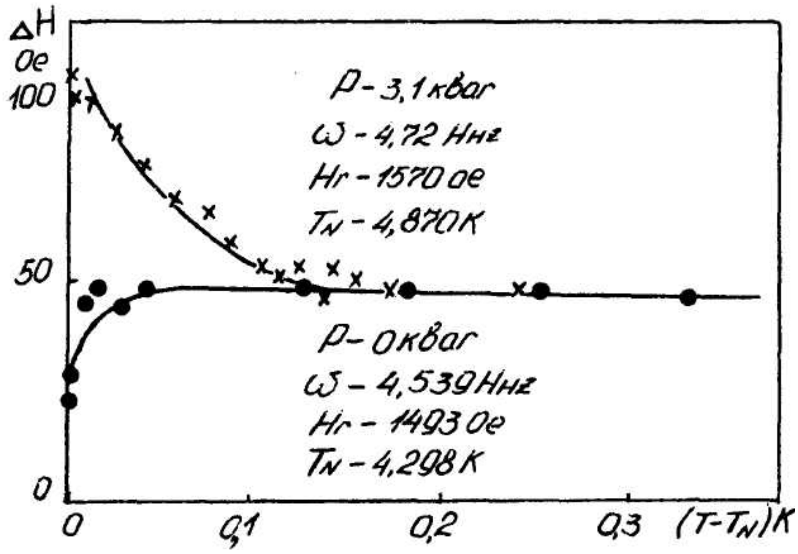

Figure 3.3. Dependence of half-width of EPR lines on (T-T_p) distance in $CuCl_2{\cdot}2H_2O$ at varied pressures [64].

Similar investigation of pressure dependence of T_p was done for $CuCl_2{\cdot}2D_2O$ single crystal [65]. For P=0, EPR study of $CuCl_2{\cdot}2D_2O$ gave T_p=4.148 K. The reduction of the temperature indicates that deuterium substitution for hydrogen results in the decrease of the value of intersublattice exchange interaction between copper ions. The reduction of the value of indirect exchange interaction can result from deuteration and expansion of $CuCl_2{\cdot}2D_2O$ lattice along $\bar{b}$ and $\bar{c}$ axis in comparison with $CuCl_2{\cdot}2H_2O$ case. Our result for relative T change in deuterated single crystal agrees well with results of [69] stating that deuteration gives 3-3.5 % decrease of T as compared with the case of the aqueous crystal.

EPR data can be used for evaluation of q-factor for $CuCl_2{\cdot}2H_2O$. In this case, the external field was oriented along $\bar{a}$ axis of the crystal, too. For the frequency ν=2.2054 GHz under zero pressure, EPR was observed at H=0.727 kOe. At these values, q-factor is equal to 2.167 which is close to that of $CuCl_2{\cdot}2H_2O$. For P=2.3 kbar, EPR was observed at ν=2.1036 GHz in the field H=0.698 kOe. Hence, q-factor equals 2.154. In such way, q-factor decreases with the rise of the pressure both in $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$.

In both the crystals, at temperatures higher of T_p, the half-width of EPR lines was diminishing with pressure increase. EPR line half-widths for zero pressure are close to those of [66, 70].

Basing on $T_p(P)$ dependence, the temperature derivative with respect to the pressure dT_p/dp =0.180 kbar for $CuCl_2{\cdot}2D_2O$. dT_p/dp of deutorated sample turned out to be lower than that of $CuCl_2{\cdot}2H_2O$. This result complies with NMR data [71] obtained under the measurement of $T_p(P)$ dependence. In [71],

$CuCl_2 \cdot 2D_2O$ dT_p/dp was equal to 0.172 K·kbar and was lower than that obtained for copper chloride dehydrate by the same method.

The uniform compression affects, first of all, the interplanar spacings in the crystal and the value of magnetic exchange interaction as follows from $T_p(P)$ evolution and it influences also resonance properties, phase transitions and other parameters of AFM.

3.3. Conclusions

The current approach to the problem of low-temperature magnetism, resonance absorption, theory, first-order structural phase transition together with single-crystal symmetry has required the copper chloride dehydrate crystal to be taken as an object of investigations. It is a low-temperature magneto-dielectric with D_{12}^{7} - P_{emn} symmetry group and the lowest rhombic system without axis of the order higher than the second one. It is a rhombic bipyramidal crystal with two H_2O molecules in the unit cell. Copper ions have orthorhombic symmetry in the crystal structure.

The studies of hydrostatic pressure effect on the changes of the structure made by X-ray diffraction method have shown that the uniform compression changes the elastic parameters of the structure and as a consequence, the energy of interactions through the mechanisms of elastic stresses with the symmetry remained unchanged. This fact is explained by the changes of thermodynamic parameters.

The compressibility of the hydrated single crystals was investigated by using X-ray diffractometer at room temperature. The linear pressure dependences of interplanar distances have been determined.

The compressibility factors have been determined for the corresponding crystallographic axes a, b, c of the orthorhombic structure. With the known compressibility factors, it is possible to use the energy of elastically deforming stresses in the expression presenting the interaction energies.