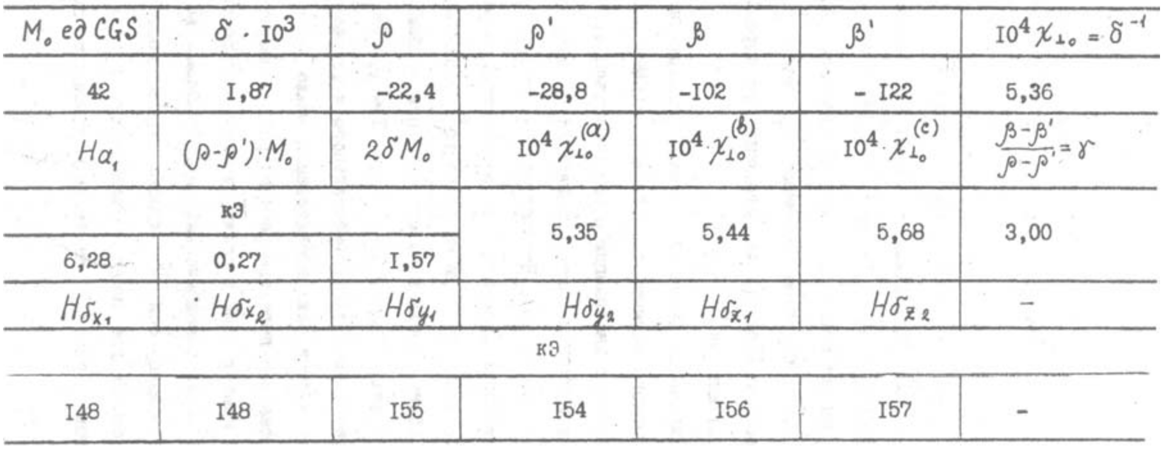
Chapter 6

Relationship between magnetoelastic and elastic properties of orthorhombic magnetodielectrics

Multiple experimental results obtained by resonance methods possess rich information on the properties of $CuCl_2 \cdot 2H_2O$ and the values of typical parameters of this magnetodielectric [49, 53, 63, 68, 71] listed in Table 1. The peculiarities of the resonance studies in the region of the structural phase transition [6] are the fact, which has been proved experimentally. In the external field parallel to a-axis, in the region of the low-frequency branch, the resonance absorption is of a specific type. There are two resonance absorption lines, one of which corresponds to the value of the resonance field equal to the resonance magnetic field at low frequencies. It is the value corresponding in the magnitude to the filed of the first-order PT. The authors of related the lines of the high-frequency field energy absorption to two phase states.

Among important generalizing characteristics of magnet-containing media, there are magnetostriction parameters and dependencies of the structural changes of properties on the hydrostatic pressure. So, the role of elastic stresses in compressible structures can de determined and shown. The influence of the pressure on the high-frequency properties, fields of the phase states, critical temperatures of the structural phase transitions and the linear dependence of the mentioned parameters on the pressure make us to conclude that both dP/dH and dTp/dP , the same as changes of the critical line of the first-order phase transition Tp(H) are of positive sign.

Table 6.1.



M_0 ед CGS	$\delta \cdot 10^3$	ρ	ρ'	β	β'	$10^4 \chi_{\perp 0} = \delta^{-1}$
42	I,87	-22,4	-28,8	-I02	- I22	5,36
Ha_1	$(\rho-\rho') \cdot M_0$	$2\delta M_0$	$10^4 \chi_{\perp 0}^{(a)}$	$10^4 \cdot \chi_{\perp 0}^{(b)}$	$10^4 \cdot \chi_{\perp 0}^{(c)}$	$\frac{\beta-\beta'}{\rho-\rho'} = \gamma$
	кЭ		5,35	5,44	5,68	3,00
6,28	0,27	I,57				
$H\delta_{x_1}$	$H\delta_{x_2}$	$H\delta_{y_1}$	$H\delta_{y_2}$	$H\delta_{z_1}$	$H\delta_{z_2}$	–
			кЭ			
I48	I48	I55	I54	I56	I57	-

Pressure effect on the magnetic properties is conditioned by magnetostriction. That is why the total parameters describing the influence can be useful for studying the magnetoelastic properties of $CuCl_2{\cdot}2H_2O$. The theoretical analysis of magnetoelastic properties of orthorhombic magnetodielectrics gives us a possibility to derive expressions for finding the magnetostriction constants [64].

The density of the free energy of magnetically ordered crystal can be represented as

$$\omega = \omega_m + \omega_{me} + \omega_e \qquad (1)$$

where $\omega_m, \omega_{me}, \omega_e$ are the densities of magnetic, magnetoelastic, elastic energy, respectively.

The density of the elastic energy of $D_{2h}^{\ 7}$ symmetry group crystals in the double sublattice model is [126]:

$$\omega_m = \frac{1}{2}A_0 M^2 + \frac{1}{2}B_0 L^2 + \frac{1}{2}\left(a_{10}M_x^2 + a_{20}M_y^2 + b_{10}L_y^2\right) - \vec{M}\vec{H} - k_B T\left[S\left(M_1\right) + S\left(M_2\right)\right] + \omega_m^{(ex)} \qquad (2)$$

Here $\vec{M} = \vec{M}_1 + \vec{M}_2$ is the vector of weak thermomagnetic moment, $L = \vec{M}_1 - \vec{M}_2$ is the vector of ferromagnetism, M_1, M_2 are the magnetizations of sublattices, A_0, B_0 are dimensionless constants of the uniform exchange interaction, $a_{10}, a_{20}, b_{10}, b_{20}$ are dimensionless constants of anisotropy, $\vec{H}$ is the external constant magnetic field, $S(M)$ is the entropy correspondingto the magnetic moment $\vec{M}$:

$$S(M) = v_0^{-1} \int\limits_{M/M_0}^{1} B^{-1}\left(x\right)dx \qquad (3)$$

where v_0 is the volume of crystal unit cell, M_0 is sublattice magnetization at the absolute zero, $B^{-1}\left(x\right)$ is the inverse Brillouin function and k_B is Boltzmann's constant.

The term $\omega_m^{(ex)}$ describes the non-uniform exchange energy and it has a standard form [126]. The constants A_0, B_0, $a_{10}, a_{20}, b_{10}, b_{20}$ are related to the exchange and anisotropy constants by which the energy of two-axis magnetodielectrics [127] is written as

$$\begin{aligned} A_0 &= \frac{1}{2}\delta; \quad a_{10} = \frac{1}{2}(\beta+\beta'); \quad b_{10} = \frac{1}{2}(\beta-\beta'); \\ B_0 &= \frac{1}{2}\delta; \quad a_{20} = \frac{1}{2}(\rho+\rho'); \quad b_{20} = \frac{1}{2}(\rho-\rho'); \end{aligned} \tag{4}$$

The density of the magnetoelastic energy can be written down in the form

$$\omega_{me} = \frac{1}{2}\Lambda_{\alpha\beta\rho\mu}u_{\alpha\beta}L_\rho L_\mu + \frac{1}{2}\tilde{\Lambda}_{\alpha\beta\rho\mu}u_{\alpha\beta}M_\rho M_\mu + \frac{1}{2}\Lambda^{(e)}_{\alpha\beta}u_{\alpha\beta}L^2 + \frac{1}{2}\tilde{\Lambda}^{(e)}_{\alpha\beta}u_{\alpha\beta}M^2 \tag{5}$$

The tensors $\Lambda_{\alpha\beta\rho\mu}$ and $\tilde{\Lambda}_{\alpha\beta\rho\mu}$ describe the relativistic magnetoelastic interactions, the tensors $\Lambda^{(e)}_{\alpha\beta}$ and $\tilde{\Lambda}^{(e)}_{\alpha\beta}$ describe the exchange magnetoelastic interactions. The doubly repeated indices imply summation. There are no terms like $\Lambda_{\alpha\beta\rho\mu}$, $u_{\alpha\beta}L_\rho M_\beta$ since in $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$, the unit cell is doubled as compared to the chemical one moreover such combinations are impossible because the sublattice atoms change places with each other during the translation and $\vec{L}$ changes its sign. The structure of tensors Λ and $\tilde{\Lambda}$ is totally determined by the symmetry of the crystal that is non-zero elements Λ and $\tilde{\Lambda}$ are those with which there are combinations of strain tensor components and components of vectors of antiferromagnetism, all being invariant with respect to all the transformations of D_{2h}^7 symmetry group. Here and below, the indices written in Greek are for writing down the components of vectors and tensors in Cartesian coordinate system, so they take values from 1 to 3. The indices written in Latin are for tensors in Feught designations, they take the values from 1 to6. The Cartesian indices relate to Feught indices as follows:

Cartesian indices	xx	yy	zz	yz	xz	xy
Feught indices	1	2	3	4	5	6

If we rewrite (5) in Feught designations, we get

$$\omega_{me} = \frac{1}{2}\Lambda_{ik}u_i L_k^2 + \frac{1}{2}\tilde{\Lambda}_{ik}u_i M_k^2 + \frac{1}{2}\Lambda^{(e)}_{\alpha}u_\alpha L^2 + \frac{1}{2}\tilde{\Lambda}^{(e)}_{\alpha}u_\alpha M^2 \tag{6}$$

Here we took the following designations: $L_1^2 = L_x^2$, $L_2^2 = L_y^2$, $L_3^2 = L_z^2$, $L_4^2 = L_y L_z$, $L_5^2 = L_x L_z$, $L_6^2 = L_x L_y$, the designations for M_k^2.

For (6), the tensors of exchange striction have only three components other than zero. The tensor of relativistic striction satisfying the properties of D_{2h}^7

symmetry group is defined by nine independent magnetoelastic constants and is of the form

$$\lambda_{ik} = \begin{pmatrix} \lambda_1 & \lambda_3 & \lambda_5 & 0 & 0 & 0 \\ \lambda_2 & \lambda_4 & \lambda_6 & 0 & 0 & 0 \\ -(\lambda_1+\lambda_2) & -(\lambda_3+\lambda_4) & -(\lambda_5+\lambda_6) & 0 & 0 & 0 \\ 0 & 0 & 0 & 4\lambda_9 & 0 & 0 \\ 0 & 0 & 0 & 0 & 4\lambda_8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4\lambda_7 \end{pmatrix} \tag{7}$$

The structure of $\tilde{\Lambda}_{ik}$ tensor is analogous to (7).

Next, for the study of magnetoelastic properties under external pressure, we write down the density of magnetoelastic energy in terms of stress tensor $\sigma_{\alpha\beta}$ using [128]:

$$\omega_e = \frac{1}{2} c_{ik} u_i u_k = \frac{1}{2} \tilde{K}_{ik} \sigma_i \sigma_k \tag{8}$$

where c_{ik} is the tensor of elastic moduli, $\tilde{K}_{ik}$ id the tensor of moduli of elastic compliance. As known, $\tilde{K}_{ik}$ is reverse to c_{ik} tensor. The structure of c_{ik} tensor for rhombic crystal is given in [128].

The tensor of moduli of elastic compliance can be written in the form

$$\tilde{K}_{ik} = \begin{pmatrix} K_{11} & K_{12} & K_{13} & 0 & 0 & 0 \\ K_{12} & K_{22} & K_{23} & 0 & 0 & 0 \\ K_{13} & K_{23} & K_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & 4K_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & 4K_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & 4K_{66} \end{pmatrix} \tag{9}$$

Using the relationship

$$u_i = \tilde{K}_{ik} \sigma_k \tag{10}$$

and substituting (10) into(5), we have

$$\omega_{me} = \frac{1}{2} Z_{ik} L_k^2 \sigma_i + \frac{1}{2} \tilde{Z}_{ik} M_k^2 \sigma_i + \frac{1}{2} Z_\alpha^{(e)} \sigma_\alpha L^2 + \frac{1}{2} \tilde{Z}_\alpha^{(e)} \sigma_\alpha M^2 \qquad (11)$$

In this expression, we have already the stress tensors, and new tensors of magnetoelastic constants Z_{ik}, $\tilde{Z}_{ik}$, $Z_{ik}^{(e)}$, $\tilde{Z}_{ik}^{(e)}$ are related to those in (6) through the following relationships:

$$\begin{aligned} Z_{ik} &= \Lambda_{mi} \tilde{K}_{mk}; \qquad & \tilde{Z}_{ik} &= \tilde{\Lambda}_{ji} K_{jk}; \\ Z_\alpha^{(e)} &= \Lambda_\beta^{(e)} \tilde{K}_{\beta\alpha}; \qquad & \tilde{Z}_\alpha^{(e)} &= \tilde{\Lambda}_\beta^{(e)} K_{\beta\alpha} \end{aligned} \qquad (12)$$

Thus, the total density of the free energy of orthorhombic AFM is of the form

$$\begin{aligned} \omega = {} & \frac{1}{2} A_0 M^2 + \frac{1}{2} B_0 L^2 + \frac{1}{2}\left(a_{10} M_x^2 + a_{20} M_y^2 + b_{10} L_x^2 + b_{20} L_y^2\right) - k_B T \left[S\left(M_1\right) + S\left(M_2\right) \right] - \\ & - \vec{M}\vec{H} + \frac{1}{2}\left[Z_{0ik} L_k^2 + \tilde{Z}_{0ik} M_k^2 \right] \sigma_i + \left[Z_{0\alpha}^{(e)} L^2 + Z_{0\alpha}^{(e)} M^2 \right] \sigma_\alpha + \frac{1}{2} \tilde{K}_{ik} \sigma_i \sigma_k - k_B T S(\sigma) \end{aligned} \qquad (13)$$

The last term of (13) describes the entropy of the lattice including the stresses σ. Going over from magnetization M and the vector of antiferronmagnetism $\vec{L}$ of the unit volume to the magnetization $\vec{\mu} = \vec{\mu}_1 + \vec{\mu}_2$ and the vector of antiferromagnetism of the unit cell $\vec{l} = \vec{\mu}_1 - \vec{\mu}_2$ for the free energy of orthorhombic AFM per one gram/mole we obtain

$$\begin{aligned} \frac{F}{N_0} = {} & \frac{1}{2} A\mu^2 + \frac{1}{2} Bl^2 + \frac{1}{2}\left(a_1 \mu_x^2 + a_2 \mu_y^2 + b_1 l_x^2 + b_2 l_y^2\right) - \vec{\mu}\vec{H} - \\ & - k_B T \left[\mathbb{S}\left(\mu_1\right) + \mathbb{S}\left(\mu_2\right) \right] + \frac{1}{2}\left[Z_{ik} l_k^2 + \tilde{Z}_{ik} \mu_k^2 \right] \sigma_i + \frac{1}{2} v_0 \tilde{K}_{ik} \sigma_i \sigma_k - \\ & - k_B T \mathbb{S}\left(\sigma\right) + \frac{1}{2}\left[Z_\alpha^{(e)} l^2 + Z_\alpha^{(e)} \mu^2 \right] \sigma_\alpha \end{aligned} \qquad (14)$$

Here $A = \dfrac{A_0}{v_0}$, $B = B_0 v^{-1}$ etc., $Z_{ik} = Z_{0ik} v_0^{-1}$, $\mathbb{S}\left(\mu_1\right) = v_0 S(M_1)$, N_0 is Avogadro number. The values of unit cell magnetization are related to spins of ions as follows

$$\vec{\mu} = g\mu_B\left(\vec{S}_1 + \vec{S}_2\right), \quad \vec{l} = g\mu_B\left(\vec{S}_1 - \vec{S}_2\right) \qquad (15)$$

where g is Lande splitting factor and μ_B is Bohr magneton.

The equilibrium values of strain, magnetization and the vector of ferromagnetism are found from the system of equations

$$u_i = \frac{\partial F}{\partial \sigma_i}; \quad \frac{\partial F}{\partial \mu_\alpha} = 0; \quad \frac{\partial F}{\partial l_\alpha} = 0 \tag{16}$$

Using the expression for the free energy of a magnetodielectric (14), we have the first equation of the system (16) in the form

$$u_i = v_0 \tilde{K}_{ik} \sigma_k - k_B T \frac{\partial \mathbb{S}(\sigma)}{\partial \sigma_i} + \frac{1}{2}\left[Z_{ik} l_k^2 + \tilde{Z}_{ik} \mu_k^2 \right] + \left[Z_\alpha^{(e)} l^2 + \tilde{Z}_\alpha^{(e)} \mu^2 \right] \delta_{i\alpha} \tag{17}$$

The second and the third equations in (16) define both the vectors of magnetization and ferromagnetism and their dependence on the stresses:

$$A\vec{\mu} + a_1 \mu_x \vec{I}_x + a_2 \mu_y \vec{I}_y - H + k_B T \left\{ B^{-1}\left(\frac{\mu_1}{\mu_0}\right) \frac{\vec{\mu} + \vec{l}}{2\mu_1 \mu_0} + B^{-1}\left(\frac{\mu_2}{\mu_1}\right) \frac{\vec{\mu} - \vec{l}}{2\mu_2 \mu_0} \right\} + \frac{1}{2} \tilde{Z}_{ik} \sigma_i \frac{\partial \mu_k^2}{\partial \vec{\mu}} + Z_\alpha^{(e)} \sigma_\alpha \vec{\mu} = 0; \tag{18}$$

$$B\vec{l} + b_1 l_x \vec{I}_x + b_2 l_y \vec{I}_y + k_B T \left\{ B^{-1}\left(\frac{\mu_1}{\mu_0}\right) \frac{\vec{\mu} + \vec{l}}{2\mu_1 \mu_0} - B^{-1}\left(\frac{\mu_2}{\mu_1}\right) \frac{\vec{\mu} - \vec{l}}{2\mu_2 \mu_0} \right\} + \frac{1}{2} Z_{ik} \sigma_i \frac{\partial l_k^2}{\partial l} + Z_\alpha^{(e)} \sigma_\alpha \vec{l} = 0 \tag{19}$$

Here $\vec{I}_x$, $\vec{I}_y$ are the unit vectors aligned with x,y-axis. The derivatives $\partial l_k^2 / \partial l_0$ are determined by the expressions

$$\begin{aligned} &\frac{\partial l_1^2}{\partial \vec{l}} = 2 l_x \vec{I}_x; \quad \frac{\partial l_2^2}{\partial \vec{l}} = 2 l_y \vec{I}_y; \quad \frac{\partial l_3^2}{\partial \vec{l}} = 2 l_z \vec{I}_z; \quad \frac{\partial l_4^2}{\partial \vec{l}} = l_z \vec{I}_y + l_y \vec{I}_y; \\ &\frac{\partial l_5^2}{\partial \vec{l}} = l_z \vec{I}_z + l_z \vec{I}_z; \quad \frac{\partial l_6^2}{\partial \vec{l}} = l_y \vec{I}_x + l_x \vec{I}_y; \end{aligned} \tag{20}$$

The derivatives $\partial \mu_i / \partial \mu$ are found in the analogous way.

By the known tensor of the crystal strain, the magnetostriction value is easily found as a function of any direction in the crystal.

$$\frac{\delta a}{a} = \frac{|\vec{a}| - |\vec{a}_0|}{|\vec{a}|} = u_{\alpha\beta}\left(\vec{l}, \vec{m}\right) n_\alpha n_\beta \tag{21}$$

where $\vec{a}_0$, $\vec{a}$ is a vector in the crystal prior to and after the magnetic ordering, respectively; $\vec{n} = \vec{a}_0 a_0^{-1}$ is the unit vector in $\vec{a}_0$ direction.

The most important and interesting case relates to magnetostriction in the absence of the external stresses $\left(\sigma_i = 0\right)$. For this case, expression (21) takes the form

$$\frac{\delta a}{a} = \frac{1}{2}\left\{Z_{\alpha\beta\gamma\delta} l_\gamma l_\delta + \tilde{Z}_{\alpha\beta\gamma\delta}\mu_\gamma\mu_\delta + \left(Z_\alpha^{(e)} l^2 + \tilde{Z}_\alpha^{(e)}\mu^2\right)\delta_{\alpha\beta}\right\} n_\alpha n_\beta \tag{22}$$

For instance, this formula describes the relative changes of the lattice parameters due to the magnetostriction. To determine the magnetostriction constants $Z, \tilde{Z}, Z^{(e)}, \tilde{Z}^{(e)}$, the magnetostriction along the ribs and diagonals of the parallelepiped should be known. The formulas are collected in Table 2.

The relative bulk magnetostriction is

$$\frac{\delta a}{a} = \left(\frac{\delta a}{a}\right)_{100} + \left(\frac{\delta a}{a}\right)_{010} + \left(\frac{\delta a}{a}\right)_{001} \tag{23}$$

Table 2.

n_α	$\delta a/a$
100	$\frac{1}{2}\left\{Z_{xx\gamma\delta} l_\gamma l_\delta + Z_x^{(e)} l^2 + \tilde{Z}_{xx\gamma\delta}\mu_\gamma\mu_\delta + \tilde{Z}_x^{(e)}\mu^2\right\}$
010	$\frac{1}{2}\left\{Z_{yy\gamma\delta} l_\gamma l_\delta + Z_y^{(e)} l^2 + \tilde{Z}_{yy\gamma\delta}\mu_\gamma\mu_\delta + \tilde{Z}_y^{(e)}\mu^2\right\}$
001	$\frac{1}{2}\left\{Z_{zz\gamma\delta} l_\gamma l_\delta + Z_z^{(e)} l^2 + \tilde{Z}_{zz\gamma\delta}\mu_\gamma\mu_\delta + \tilde{Z}_z^{(e)}\mu^2\right\}$
$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{1}{2}\left\{\left(\frac{\delta a}{a}\right)_{100} + \left(\frac{\delta a}{a}\right)_{010}\right\} + \frac{1}{2}\left\{Z_{xy\gamma\delta} l_\gamma l_\delta + \tilde{Z}_{xy\gamma\delta}\mu_\gamma\mu_\delta\right\}$
$\frac{1}{\sqrt{2}}\ 0\ \frac{1}{\sqrt{2}}$	$\frac{1}{2}\left\{\left(\frac{\delta a}{a}\right)_{100} + \left(\frac{\delta a}{a}\right)_{001}\right\} + \frac{1}{2}\left\{Z_{xz\gamma\delta} l_\gamma l_\delta + \tilde{Z}_{xz\gamma\delta}\mu_\gamma\mu_\delta\right\}$
$0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}$	$\frac{1}{2}\left\{\left(\frac{\delta a}{a}\right)_{010} + \left(\frac{\delta a}{a}\right)_{001}\right\} + \frac{1}{2}\left\{Z_{yz\gamma\delta} l_\gamma l_\delta + \tilde{Z}_{yz\gamma\delta}\mu_\gamma\mu_\delta\right\}$
$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{1}{3}\left\{\left(\frac{\delta a}{a}\right)_{100} + \left(\frac{\delta a}{a}\right)_{010} + \left(\frac{\delta a}{a}\right)_{001}\right\} + \frac{1}{3}\left\{\left(Z_{xy\gamma\delta} + Z_{yz\gamma\delta} + Z_{xz\gamma\delta}\right) l_\gamma l_\delta + \left(\tilde{Z}_{xy\gamma\delta} + \tilde{Z}_{yz\gamma\delta} + \tilde{Z}_{xz\gamma\delta}\right)\mu_\gamma\mu_\delta\right\}$

If an external stress σ is applied now to the sample, then, in linear approximation, the strains due to the external stresses and magnetostriction effect are added together.

The expression for the free energy (14) consists of many phenomenological constants characterizing the magnetic, magnetoelastic and elastic energies. However, these can be found only experimentally with arbitrary components of stress tensors, variations of the direction and the value of the external magnetic field and by the measurement of the strains of any directions and the components of $\vec{l}$, $\vec{\mu}$ vectors. In such experiments, the set of data will be much larger than the set of unknown parameters in (14). It will become possible to have experimental results andtocontrolthe validity ofthre experimental data and the theoretical statements.

$CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$ crystals are very brittle, so it is very difficult to study them experimentally. A question arises of finding another way to determine the parameters, which describe the free energy of the crystal. Thus, in [50], the components of the tensors of elastic-compliance moduli for the orthorhombic $CuCl_2 \cdot 2H_2O$ have been found by measuring the sound velocity in the crystal.

Another convenient external parameter that influences AFM properties,is hydrostatic pressure. It has been shown that the magnetic properties of $CuCl_2 \cdot 2H_2O$, i.e. Neel temperature, the field of sublattice magnetic moment flip-flop, frequencies depend on the pressure very strongly. The pressure dependences of the basic magnetic characteristics of the crystal, i.e. $T_N = T_N(P),\ H_n = H_n(P),\ \omega_r = \omega_r(P)$ and so on can be used to determine some combinations of magnetoelasticconstants for this dependence is conditioned by magnetoelastic interactions present in the crystal.

This effect can be traced better in the case of the hydrostatic pressure that is when the stress tensor can be represented as $\sigma_k = \left\{ \frac{1}{3}P, \frac{1}{3}P,\ \frac{1}{3}P,\ 0,\ 0,\ 0 \right\}$. At the given σ_k, the magnetostriction energy takes the form analogous to the expression for the magnetic energy (see (14)). Therefore, it is possible to describe the influence of the external pressure by a simple renormalization of the constants of the energy magnetic part

$$\frac{F_m}{N_0} = \frac{1}{2}\tilde{A}\mu^2 + \frac{1}{2}\tilde{B}l^2 + \frac{1}{2}\left(\tilde{a}_1\mu_x^2 + \tilde{a}_2\mu_y^2 + \tilde{b}_1 l_x^2 + \tilde{b}_2 l_y^2\right) - \vec{\mu}\vec{H} + k_B T\left[\mathbb{S}\left(\mu_1\right) + \mathbb{S}\left(\mu_2\right)\right] \quad (24)$$

Here

$$\begin{gathered}
\tilde{A} = A + \frac{1}{3} P \sum_{\alpha=1}^{3} \left(\tilde{Z}_{\alpha}^{(e)} + \tilde{Z}_{\alpha 3} \right) \equiv A + \frac{1}{3} P \tilde{L}^{(e)} \\
\tilde{B} = B + \frac{1}{3} P \sum_{\alpha=1}^{3} \left(\tilde{Z}_{\alpha}^{(e)} + \tilde{Z}_{\alpha 3} \right) \equiv B + \frac{1}{3} P \tilde{L}^{(e)} \\
\tilde{a}_1 = a_1 + \frac{1}{3} P \sum_{\alpha=1}^{3} \left(\tilde{Z}_{\alpha 1} - \tilde{Z}_{\alpha 3} \right) \equiv a_1 + \frac{1}{3} P \tilde{L}_1 \\
\tilde{a}_2 = a_2 + \frac{1}{3} P \sum_{\alpha=1}^{3} \left(\tilde{Z}_{\alpha 2} - \tilde{Z}_{\alpha 3} \right) \equiv a_2 + \frac{1}{3} P \tilde{L}_2 \\
\tilde{b}_1 = b_1 + \frac{1}{3} P \sum_{\alpha=1}^{3} \left(\tilde{Z}_{\alpha 1} - \tilde{Z}_{\alpha 3} \right) \equiv b_1 + \frac{1}{3} P \tilde{L}_1 \\
\tilde{b}_2 = b_2 + \frac{1}{3} P \sum_{\alpha=1}^{3} \left(\tilde{Z}_{\alpha 2} - \tilde{Z}_{\alpha 3} \right) \equiv b_2 + \frac{1}{3} P \tilde{L}_2
\end{gathered} \tag{25}$$

In such a way, the external hydrostatic pressure results in the renormalization of exchange and anisotropy constant, the combination of which affects such parameters as Neel temperature, the field of the sublattice magnetic moment flip-flop, the resonance frequency? The temperature of the triple point of the phase (H-T) diagram, etc. The above-mentioned parameters are pressure-dependent and the combinations of magnetostriction constants can be determined from the experimental pressure dependences. The expressions relating the parameters with the anisotropy and the exchange constants are of the form [129]:

$$T_N = \frac{2\mu_B^2}{k_B} \left| \tilde{B} \right| \tag{26}$$

$$T_3 = T_N - \frac{3\mu_B^2}{k_B} \tilde{b}_2 \tag{27}$$

$$H_n^2 = \mu_B^2 \tilde{b}_2 \left(\tilde{A} - \tilde{B} - b_2 \right) \left(\frac{\mu(T)}{\mu_B} \right)^2 \tag{28}$$

Here the fact that for $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2D_2O$ the copper ion spin $s = 1/2$ has been taken into account and g-factor can be considered to be equal to 2. $\mu(T)$ is the magnetization of the sublattice at the temperature T. The field corresponding to the triple point is found from the relation $H_3 = H_n(T_3)$. The calculations of the resonance fields and angles of the resonance field separation as the functions of the frequency gave the following expressions:

$$H_r^2(\nu) = H_n^2 - \left(\frac{h\nu}{2\mu_B}\right)^2 \left(\frac{r+3}{r-1}\right) \tag{29}$$

$$\sin\psi_f(\nu) = \frac{(h\nu)^2}{(2\mu_B H_n)^2} A(r) \tag{30}$$

where $r = \tilde{b}_1 \tilde{b}_2^{-1}$ and ν is the frequency. The value $A(r)$ has the form

$$A(r) = \frac{1}{2}\left[(r+1)\left(1+b^2\right)^{1/2} + 2b\right](r-1)^{-1}\left(1+b^2\right)^{-1} \tag{31}$$

and the parameter b from this expression is equal to

$$b = (2q)^{-1}\left\{\sqrt{(q+3)^2 + 4q} - (q+3)\right\}, \qquad q = \left(\frac{r+1}{2}\right)^2 - 1 .$$

By differentiating formulas (26)-(28), we have

$$L^{(e)} = \frac{3k_B}{2\mu_B{}^2}\frac{dT}{dP} \tag{32}$$

$$2L^{(e)} - 3L_2 = \frac{3k_B}{\mu_B^2}\frac{dT_3}{dP} \tag{33}$$

$$\frac{\tilde{L}^{(e)} - L^{(e)}}{A-B} + L_2\left(\frac{1}{b_2} - \frac{1}{A-B}\right) = \frac{6}{H_n}\frac{dH_n}{dP} \tag{34}$$

With formulas (32)-(34) and the known experimental dT_N/dP, dT_3/dP dH_n/dP values, we find the combinations of magnetoelastic constants denoted by $\tilde{L}^{(e)}$, $L^{(e)}$, L_2. Formulas (29), (31) are used for writing down an expression for insufficient combination of magnetoelastic constants

$$\begin{aligned} L_1 - r_0 L_2 &= 3b_2 \frac{(r_0-1)^2}{2}\left(\frac{\gamma}{\nu}\right)^2 \left[H_r' H_r - H_n' H_n\right] = \\ &= \frac{3b_2}{A'(r_0)}\left\{\left(\frac{rH_n}{\nu}\right)^2 \psi_f' \cos\psi_f + \frac{2H_n{}'}{H_n} A(r_0)\right\} \end{aligned} \qquad (35)$$

Here $r_0 = b_1 b_2^{-1},\ H_r' = dH_r/dP,\ H_n' = dH_n/dP,\ \gamma = 2\mu_B/h,\ \psi_f' = d\psi_f/dP,\ A(r_0) = \left(dA(r)/dr\right)_{r=r_0}$

It should be noted hat the account of the quadratic terms with respect to pressure would have been an excessive accuracy. This is because we do not take into account the quadratic terms with respect to the stress tensor into account in the expression for the magnetoelastic energy and in (25), consequently.

Experimental investigations of $CuCl_2{\cdot}2H_2O$ and $CuCl_2{\cdot}2D_2O$ properties done under pressure have made it possible to determine typical parameters and to calculate combinations of magnetoelastic constants by (32)-(35).

The pressure dependences of Neel temperature, field of the spin-flop transition were studied by NMR[7], EPR and resonance absorption methods [64, 65, 84]. Now, we calculate magentostriction constants for two data sets. Such values as dT/dP, H_r, dH_r/dp have been determined by only one method: the former parameter was treated by NMR and the latter ones used the resonance method, respectively.

First we give the results of calculation of magnetoelastic constants by resonance absorption method. Table 3 lists the basic parameters to be used in calculations.

For $CuCl_2{\cdot}2H_2O$, the values of resonance and transition fields were taken for the temperature of 1.68 K and the frequency $\nu = 3GHz$. For the deuterated crystal, H_r and H_t have been determined for T=1.74K and $\nu = 2.206$ *GHz*. The values of the derivative with respect to pressure of the triple point were taken from [71, 130].

Using (32), (33) for the aqueous crystal, we have $L^{(e)} = 4.45{\cdot}10^{23}$ $Oe^2/erg\ .kbar$, $L_2 = 0.51{\cdot}10^{23}$ $Oe^2/erg\ .kbar$ For $CuCl_2{\cdot}2D_2O$, these parameters are $L^{(e)} = 4.33{\cdot}10^{23}$ $Oe^2/erg\ .kbar$, $L_2 = 0.42{\cdot}10^{23}$ $Oe^2/erg\ .kbar$. The decrease of the

Table 3.

AFM	$\frac{dT_N}{dP},\ \frac{K}{kbar}$	$H_n,\ kOe$	$\frac{dH_n}{dP},\ \frac{kOe}{kbar}$	$H_r,\ kOe$	$\frac{dH_r}{dP},\ \frac{kOe}{kbar}$	$\frac{dT_3}{dP},\ \frac{K}{kbar}$
$CuCl_2{\cdot}2H_2O$	0.185	6.7	0.147	6.48	0.152	0.153
$CuCl_2{\cdot}2D_2O$	0.18	6.62	0.14	6.52	0.143	0.154

value of $L^{(e)}$ for the deuterated crystal is because its dT_N/dP value is lower than that for $CuCl_2 \cdot 2H_2O$. The increase of L_2 in $CuCl_2 \cdot 2D_2O$ is because dT_3/dP is higher than in the aqueous crystal.

For getting the totality of the magnetoelastic constants, the values of AFM constants (A,B) and b_2 should be known. They are found from (4) and the parameters of the uniform part of AFM Hamiltonian. From (34), it follows for $CuCl_2 \cdot 2H_2O$ $\tilde{L}^{(e)} = -2.8 \cdot 10^{25}\ Oe^2/erg \cdot kbar$, and for $CuCl_2 \cdot 2D_2O$ $\tilde{L}^{(e)} = -2.3 \cdot 10^{25}\ Oe^2/erg \cdot kbar$. The decrease of the amount of the magnetoelastic constants for the deuterated sample is due to the lower (A-B) and b_2 (because of the unit cell tension under deuteration) and lower H_r and H_t and their derivatives with respect to pressure, as compared to those for the aqueous crystal.

When calculating the latter set of magnetostriction constants L_1, we considered that $r_0=3$ to be the same for the both samples. For $CuCl_2 \cdot 2H_2O$, we find by (35) $L_1 = 1.53 \cdot 10^{23}\ Oe^2/erg \cdot kbar$ and for $CuCl_2 \cdot 2D_2O$ $L_1 = 1.27 \cdot 10^{23}\ Oe^2/erg \cdot kbar$.

Now let us to calculate the same values using the data of Table 4 based on NMR [71].

The values of all the fields are for T=2 K, the value of the resonance field and dH_r/dP are taken for $CuCl_2 \cdot 2H_2O$ at 3 GHz frequency [121], those for $CuCl_2 \cdot 2D_2O$ [65] for $\nu = 2.206\ GHz$. As a result, we have the following values for the amount of magnetostriction constants (Table 5).

While comparing the values of magnetically ordered constants calculated with two data sets, it can be concluded that in the both cases, the magnetoelastic constants for the deuterated crystal are lower than those for the aqueous one.

Table 4.

AFM	$\frac{dT_N}{dP}, \frac{K}{kbar}$	H_n, kOe	$\frac{dH_n}{dP}, \frac{kOe}{kbar}$	H_r, kOe	$\frac{dH_r}{dP}, \frac{kOe}{kbar}$	$\frac{dT_3}{dP}, \frac{K}{kbar}$
$CuCl_2 \cdot 2H_2O$	0.18	6.78	0.142	6.64	0.143	0.153
$CuCl_2 \cdot 2D_2O$	0.172	6.67	0.138	6.53	0.14	0.154

Table 5.

AFM	$L^{(e)}$	$\tilde{L}^{(e)}$	L_1	L_2
	$Oe^2 \cdot erg^{-1} \cdot kbar^{-1}$			
$CuCl_2 \cdot 2H_2O$	$4.34 \cdot 10^{23}$	$-2.36 \cdot 10^{25}$	$1.28 \cdot 10^{23}$	$0.43 \cdot 10^{23}$
$CuCl_2 \cdot 2D_2O$	$4.15 \cdot 10^{23}$	$-1.54 \cdot 10^{25}$	$0.86 \cdot 10^{23}$	$0.29 \cdot 10^{23}$

Conclusions

The magnetostriction constants are rather important characteristics of magnet-containing systems. The results of investigations of hydrostatic pressure effect on high-frequency magnetic properties, PT parameters enable us to show their correlation with the magnetic field effect through magnetic elasticity.

With the correlation between strain and stress parameters under the loading with hydrostatic pressure taken into account, the theory embraces the whole of interactions in magnet-containing structures. The expression for the density of magnetic energy per gram/mole includes all types of the interactions, e.g. binding energy present in the single crystal.

In the expression for the free energy, there is a large number of phenomenological constants that characterize magnetic, magnetoelastic and elastic energies. Hydrostatic pressure is the most successful parameter that influences the energies through elastic stresses. Our investigations have shown the role of uniform compression effect in the regularity of structural phase transition critical line and its influence on the high-frequency properties. As a result, we have combinations and estimates of magnetoelastic constants that define the influence of interactions of the magnetoelastic stresses.

The analysis of magnetoelastic properties is supplemented by investigations of elastic properties of hydrated crystals. The estimation of compressibility factors aids if establishing the relationship between elastic stresses and deformation of the structure to be used in the expression for the interaction energies. Complex investigations reveal the nature of elasticity mechanisms participating in formation of the first-order phase transitions in magnet-containing structures studied.