Chapter 10

Nature of bulk elasticity and its role in the formation of phase transition

The review of the numerous results taken in the previous chapters, was dedicated to the study of the properties of materials under influence of three thermodynamic parameters (temperature, magnetic field, pressure) and showed that the inclusion in the number of influencing parameters of high pressure significantly enlarges information base and it makes it possible in a new way to glance at nature of the observed phenomena.

10.1. The bulk elasticity of solid under the external influences

Study of conductivity in the simple and in the complex materials under the conditions for the joint action of three parameters: magnetic field, pressure and the temperature also in the sufficiently wide range of temperatures (to 350 K), pressures (to 1.8 GPa) and magnetic pour on (to 8 kOe) was determined the similar influence of these thermodynamic forces on the properties of materials (see chapter 8), which indicates the united mechanism of these influences. The analysis of experimental data showed that the action of temperature, magnetic field and pressure cause a linear change of the resistance properties for many materials. The influence of external actions, thanks to existence of cross effects (thermoelasticity, magnetic piezoelectric effect) leads to volume change too.

Changes in the properties and volume are linear and reversed behavior over a wide range acting parameters. So it can be the properties being investigated are depended by the bulk elasticity of solid? Which nature of this connection? What mechanism of the effect of temperature, magnetic field, pressure on the properties?

According to main principles of thermodynamics [222, 223] the state function of an arbitrary volume of a solid (free Gibbs energy) depends on the set of operating thermodynamics parameters.

$$\Phi = U - TS - HB - \sigma\varepsilon \tag{10.1}$$

For the selected operating forces, the complete differential of the state function is

$$d\Phi = -SdT - \varepsilon_{\lambda} d\sigma_{\lambda} - B_i dH_i \tag{10.2}$$

Or in the generalized form

$$d\Phi = -x_i dX_i \tag{10.3}$$

where x_i are the generalized co-ordinates (S is the entropy, ε is the deformation, B is the magnetic induction) and X_i are the generalized thermodynamics forces (T is the temperature, H is the magnetic field, σ is the mechanical stress).

Series expansion of the generalized coordinate $x_i = \frac{\partial \Phi}{\partial X_i}$ in the Tailor's series at the equilibrium point X_{0j} in absence of magnetic, thermal and mechanical fields and consideration of the first order terms only allowed us to define the change of any parameter under the action of all forces:

$$dx_i = -\left(\frac{\partial^2 \Phi}{\partial X_i \partial X_j} \right)_0 dX_j = M_{ij} dX_j \tag{10.4}$$

where M_{ij} is the matrix of thermodynamics coefficients. Its components are as follows: $q_i = -\frac{\partial^2 \Phi}{\partial T \partial H_i}$ is the pyromagnetic coefficient; $\alpha_\lambda = -\frac{\partial^2 \Phi}{\partial T \partial \sigma_\lambda}$ is the coefficient of thermal expansion; $\chi_{ij} = -\frac{\partial^2 \Phi}{\partial H_i \partial H_j}$ is the magnetic receptivity, $b_{i\mu} = -\frac{\partial^2 \Phi}{\partial H_i \partial \sigma_\lambda}$ is the magnetostriction (piezomagnetic) coefficient, $s_{\lambda\mu} = -\frac{\partial^2 \Phi}{\partial \sigma_\lambda \partial \sigma_\mu}$ are elastic coefficients. Thus, the influence of any thermodynamics force changes other parameters of the system, and the change of even one parameter entails appearance of all three forces.

Now we select one parameter, namely deformation ε describing the change of volume. The deformation can be carried out by three ways, videlicet heating, magnetization and deformation (the hydrostatic pressure is a special case of mechanical deformation $\sigma_\lambda = \sigma_{ij} = -\delta_{ij} P$). Consequently, the deformation (and as the consequence, stressed) state of system is formed under the effect of three thermodynamic forces, each of which gives the contribution to the general state of the body in accordance with the relationship:

$$d\varepsilon_\lambda = \alpha_\lambda dT + b_{k\lambda} dH_k + s_{\lambda\mu} d\sigma_\mu \tag{10.5}$$

The first component $\alpha_\lambda dT$ describes the change of volume with the heating (thermal expansion). The second component $b_{k\lambda}dH_k$ shows a change of volume under the action of magnetic field (magnetostriction phenomenon). The term $d\varepsilon_{\lambda 3} = s_{\lambda\mu}d\sigma_\mu$ describes the deformation of body under the mechanical deforming and it is Hooke's law.

If the solid is fixed and does not have a possibility to free change of volume $d\varepsilon = 0$ then the thermoelastic stresses appears at heating of the material in the absence of magnetic field $d\sigma_\lambda = -\frac{\alpha_\lambda}{s_{\lambda\mu}}dT$ (mechanocaloric effect). The magnetic field can lead to heating of material too (magnetocaloric effect).

As this follows from (10.5), $d\varepsilon_\lambda = 0$ at the absence possibility to the free expansion and action of one of the parameters will cause a change in two rests, which reflects proceeding into solid redistribution of energy. Hence it follows that there are the necessary to compulsorily control all three parameters during experiments, but not two, as this usually is done. Thus, if body is fixed, then the stress state of solids changes under heating or under magnetic field.

However, a change in the stressed state of solid occurs also in the presence of conditions for a free change of volume under the effect of heating, magnetic field and pressure. This is caused by the following reasons. The fact is that even in the absence any external actions, energy of body is not zero. In the material is a certain stored deformation energy and “zero” internal stresses even at absolute zero. These stresses are caused as reaction on the attracted forces between the atoms, which ensure the retention of the integrity of solid body.

The stresses, caused by the external action (pressure, temperature, magnetic field) allow to regulate the volume of solid and to change its stressed state, but they are only relative small addition to the already existing zero stresses. Summary stress field are determined by the sum of internal and external stresses.

10.2. Internal “zero” stresses in the solid

The volume of solid body is determined by the existing balance of forces of attraction and repulsion between the separate atoms, when they are united into single whole. In the quantum chemistry it is assumed that the atom is the positively charged nucleus, surrounded by the electrons rotating around [224-227]. An electron in the atom is considered as electron cloud with the nonhomogenous density in the radial direction (fig 10.1).

Sizes and form of atom are determined by its electron shell. The simplest cloud form have *S*- electron (sphere). *P-, d-, f-* electrons have a form of dumbbell, four-blade or even more complex (Fig. 10.2) [227].

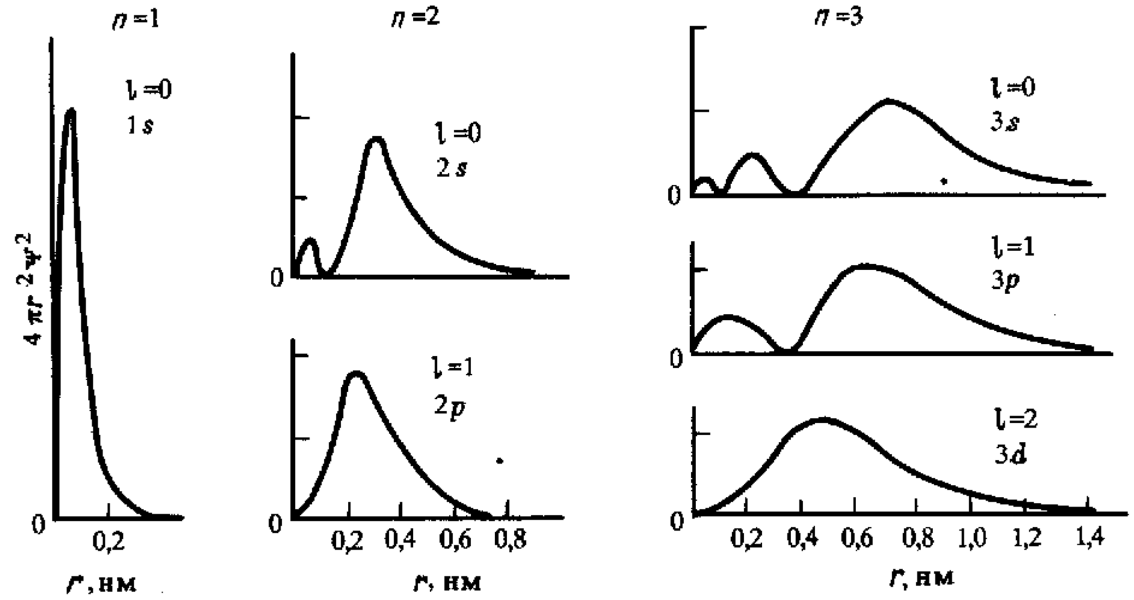


Figure 10.1. Radial distribution of density probability for electron (electron density) at a distance R from the nucleus [224].

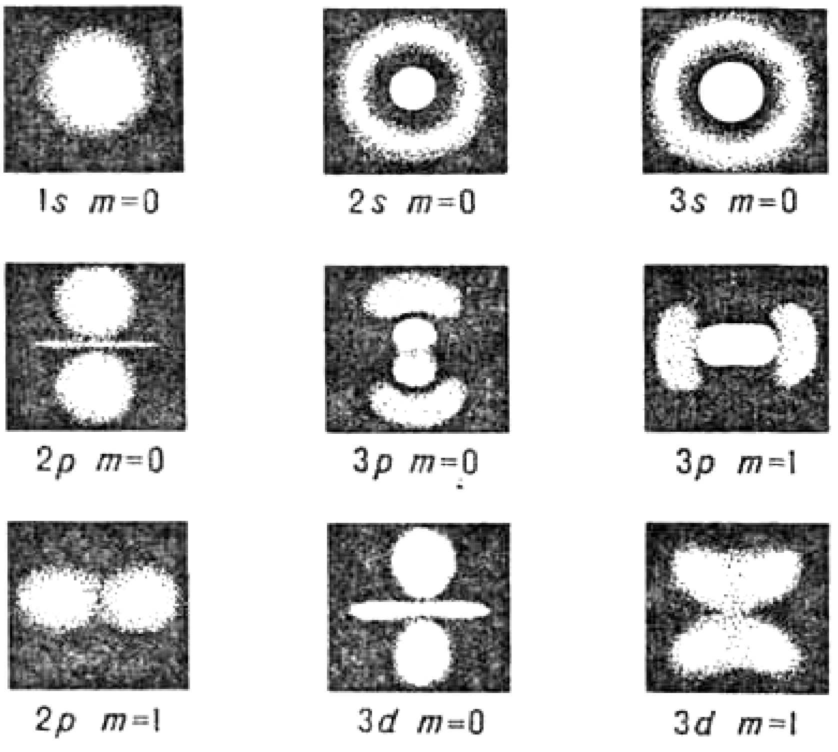

1s m=0
2s m=0
3s m=0
2p m=0
3p m=0
3p m=1
2p m=1
3d m=0
3d m=1

Figure 10.2. Form of electron clouds for different state of electron [227].

Free atom does not have clear boundaries; therefore there are several systems of the determination of the atomic radius, analysis and comparison of which is carried out in the work [228]. In some works [225, 232] the atomic radius includes 90% of electron density, while in others [229-231] it corresponds to the maximum value of electron density (fig.10.1). The results of the quantum-mechanical calculations of the orbital radius of free atoms for some elements, made works [229-232] give to table.10.1. As we see that the results of calculations differ almost two times.

In the number of works the atomic radius are determined from the data of the measurement of interatomic distances in the crystalline bodies as half of the distance between the lattice site (effective radius). It is clear, that an effective radius is always less than the sizes of free atoms, since with the formation of solid bodies the overlapping of electron orbits unavoidably occurs.

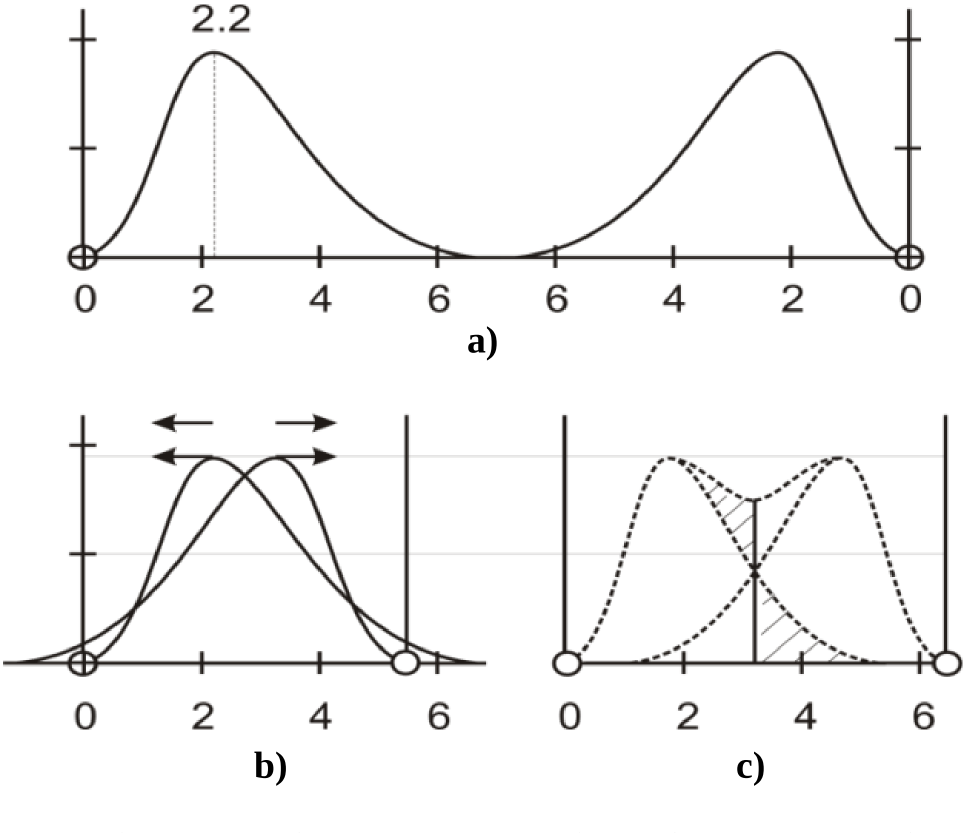
Table 10.1.

	Z		Atom radius R_0, A^o					E_o
			[229]	[230]	[231]	[232]	[233]	[233]
2	3	Li	1,45	1,58	2,37	1,5	1,67	1,0
	4	Be	1,05	1,04	1,99	0,9	1,13	1,5
	5	B	0,85	0,77	1,76	1,2	0,91	
3	11	Na	1,80	1,71	2,5	1,5	1,89	0,9
	12	Mg	1,50	1,28	2,31	0,8	1,60	1,2
	13	Al	1,25	1,31	2,28	1,0	1,43	1,5
4	19	K	2,20	2,16	2,91	1,36	2,36	0,8
	20	Ca	1,80	1,68	2,79	1,54	1,97	1,0
	21	Cs	1,60	1,57	2,67	1,63	1,64	1,36
	22	Ti	1,40	1,48	2,57	1,66	1,46	1,54
	23	V	1,35	1,40	2,49	1,55	1,34	1,63
	24	Cr	1,40	1,45	2,42	1,83	1,27	1,66
	25	Mn	1,40	1,28	2,36	1,88	1,30	1,55
	26	Fe	1,40	1,23	2,29	1,91	1,26	1,83
	27	Co	1,35	1,18	2,24	1,9	1,25	1,88
	28	Ni	1,35	1,14	2,18	1,65	1,24	1,91
	29	Cu	1,35	1,19	2,10	1,81	1,28	1,90
	30	Zn	1,35	1,06	2,10	0,8	1,39	1,65
5	37	Rb	2,35	2,29	3,04	1,3	2,48	0,8
	38	Sr	2,00	1,84	2,99	1,6	2,15	1,0
	39	Y	1,80	1,69	2,83	1,6	1,81	1,3
	40	Zr	1,55	1,59	2,72	2,16	1,60	1,6
	41	Nb	1,45	1,58	2,63	2,28	1,45	1,6
	42	Mo	1,45	1,52	2,56	2,2	1,39	2,2
	43	Tc	1,35	1,39	2,50	1,93	1,36	1,9
	44	Ru	1,30	1,41	2,44	1,69	1,34	2,2
	45	Rh	1,35	1,36	2,39	1,78	1,34	2,3
	46	Pd	1,40	0,57	2,34	1,7	1,37	2,2
	47	Ag	1,60	1,29	2,30	2,05	1,44	1,9

Free atoms enter into interaction and form the solid body at a certain distance with the rapprochement to each other. As a rule, at the atmospheric pressure and room temperatures, the simple solid are formed by the atoms of the uniform elements, which have the nonpolarized electrons. Here we are limited only of metallic materials.

The attracting forces between the atoms are included at the close distances, and the overlapping of electron clouds occurs. The covalent bond appears in the direction of the maximum overlap of electron clouds, which depends on the type of the interacting electrons and number of atoms. As a result the ordering of atoms into the crystal structure take place under the action of chemical forces and solid body is formed.

Chemical forces of interaction (attracting forces) between the neutral atoms are described by the ionization potential E_i, which characterizes energy of the electron detachment from the atom, and also the electronegativity E_o, which characterizes the capability of atom to attract electrons for itself. The increase of electronegativity E_o the element corresponds to increase the attraction force of electrons to atom. Values E_o for the row of metals are given in table. 10.1.



a)

b) c)

Figure 10.3. Diagram of the appearance of internal stresses. Overlap and the deformation of electron clouds with the rapprochement of the atoms of K a) the density of the electron cloud of free atoms; b) the overlap of orbitals in the solid; c) the addition of orbitals in the solid.

Since the atoms are not solid spheres, the deformation of the electron clouds of atoms occurs with the packing of atoms into crystal lattice; therefore the sizes of atoms in the solid are substantially less than the dimensions of free neutral atom. In Fig. 10.3 is schematically shown the distribution of the density of the electron cloud of two free atoms of potassium (fig.10.3a) and the overlap of these clouds with the rapprochement of atoms.

A probability of the detection of electrons grows in the regions of overlap. The simplest case of summary density distribution function is the addition of the functions of free atoms, whose result is shown in fig.10.3b. The general electron cloud is symmetrical because the polarization is absent for the identical atoms. As can be seen from figure 10.3, the volume of atom decreased, but the density of electron cloud increase. The stored deformation energy of atom increases also.

We see that each atom in the solid is in the compressed state, but it attempts to restore own volume. Why? Most likely because that each particle, each atom has specific volume, which, just as mass and particle charge, is a certain constant. However, in contrast to the mass and the charge, volume is not hard constant, because depends on ambient conditions, i.e., one is capable to react to the external actions, to decrease with the compression, to increase with the heating, to change its form in the magnetic field.

Obviously that the dimensions of crystal lattice and the volume of body will be determined by the balance of forces of attraction, determined by the chemical atomic bond and repulsive forces. Although, as it is assumed in chemistry, the nature of repulsive forces has electrical nature, undoubtedly, the elastic forces of electron shells have contribution to repulsion forces. The inclusion of the elastic forces of in the force balance which form solid, makes it possible to connect the together electrical, chemical and mechanical properties of solid. Nature of all properties is united and now we can find the place of mechanical properties in connection with other properties of solids.

Thus, the deformation of electron shells leads to the appearance internal stresses in the solid, which exist also at absolute zero. These “zero” stresses are the measure of the forces of chemical attraction and compensate them, determining the value of interatomic distances in crystal lattice of body. Such internal stresses are the new collective property of material, found during the association of atoms into new system as solid. Note that because orbitals often have the complex anisotropic form (fig.10.2), the amount of deformation of electron shells when the atoms pack into the lattice is different will be in the different directions. It is determines the anisotropic tensor nature of elastic properties.

Existence of correlation between the chemical bond and the elastic properties of elements could confirm the presence of internal stresses. Data of bulk modulus for the metals of 2 - 6 periods of the periodic table in accordance with the electronegativity to Pauling are given in fig. 10.4. The graph show the actually linear correlation between the attracting forces in atoms and the strength of material which, as we assume, is caused by the deformation of electron shells. The obtained dependence indicates existence of the regular connection between the chemical and elastic properties of solid bodies.

Very good correlation between the density of electron shells and the elasticity of material is observed. In Fig. 5 and 6 are shown the values of the bulk modulus and density of the electron shells ρ_d for a number of chemical elements. An estimate of the average density of electron shells is given in Table 2. The density ρ_d are executed according to formula $\rho_d = \frac{Zm_e}{V_d}$, where Z - the atomic number of element, m_e - the mass of electron, V_d - volume of the deformed atom in the lattice.

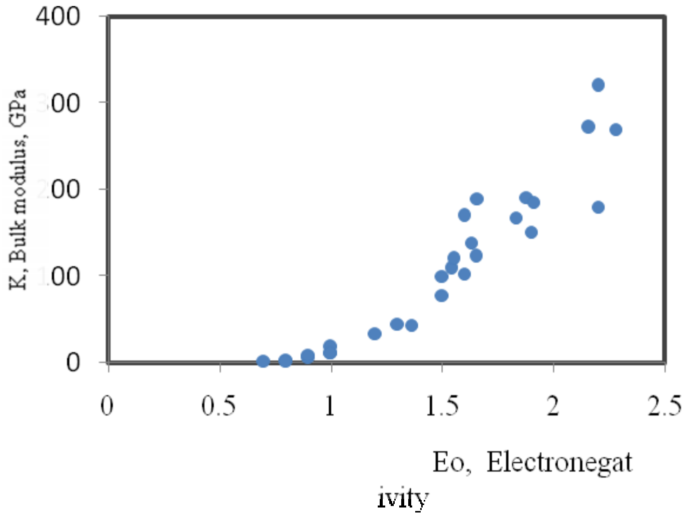


Figure 10.4. Correlation of the bulk modulus and electronegativity.

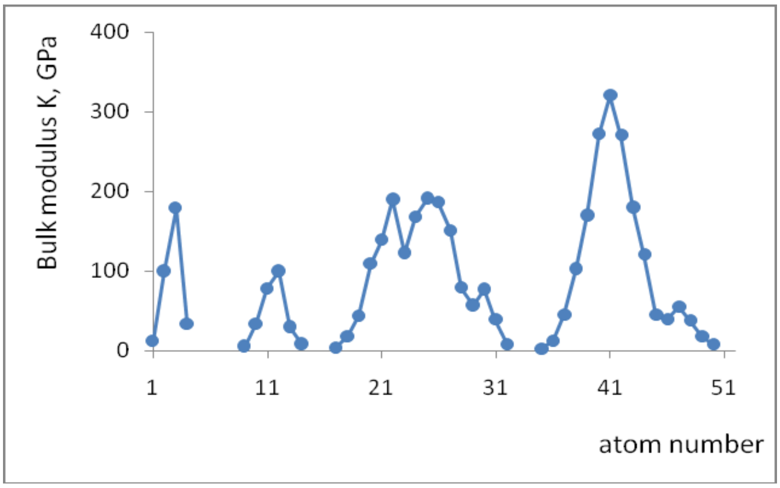


Figure 10.5. Influence of atomic number on the elastic properties of the elements.

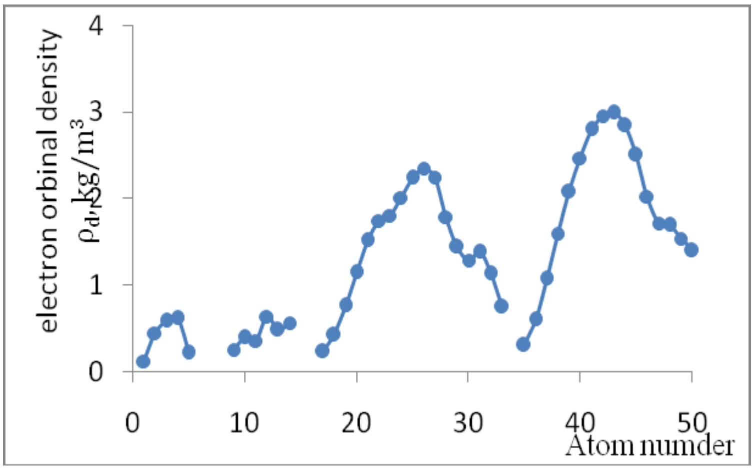


Figure 10.6. Influence of the atomic number on the density of the electron shells.

The surprising agreement of the behavior for dependences confirms the hypothesis that the density of electron shells determines the strength of the material.

10.3. Estimation of internal stresses

The values of internal stresses are sufficiently high and attain several GPa.

1. The estimation of internal stresses within the linear theory of elasticity is made on the assumption that the deformability of electron cloud correlates with the elastic properties of the material:

$$\sigma_{lm} = c_{lmik}\varepsilon_{ik} \tag{10.6}$$

where C_{lmik} are elastic modules of material. For isotropic materials we can use the simplified equation

$$\sigma_i = K\varepsilon_i \quad \text{or} \quad \sigma = K\cdot\frac{\Delta V}{V_0} \tag{10.7}$$

where K is bulk modulus (compression modulus) [234-235], $\Delta V = V_0 - V_d$ is the change of volume of free atom V_o at packing the free atom to crystal lattice (the simplest case of the spherical form of the atom is examined $V_o = \frac{4\pi}{3}R_o^3$), V_d is the volume of the deformed atom in the lattice, calculated from the data of element density $V_d = \frac{m_a}{\rho}$ (m_a is atom mass, ρ is density) .

Table 10.2.

period	Z	element	R_a, A° [3]	V_0 $10^{-30}m^3$	m_a, a.m.u.	ρ, 10^3 kg/m^3	V_d, $10^{-30}m^3$	ΔV, $10^{-30}m^3$	K, GPa	ρ_e, kg/m^3	**σ, GPa**	U_d, eV
2	3	Li	2,37	55,64	6,94	0,534	21,57	34,07	12	0,125	**7,7**	0,7
	4	Be	1,99	33,44	9,01	1,848	8,07	25,37	100	0,446	**76**	6,0
	5	B	1,76	22,76	10,81	2,34	7,67		179	0,586		5,5
	6	C				2,25	8,85		34	0,616		
	7	N				0,80	29,05			0,219		
	8	O										
	9	F										
	10	Ne										
3	11	Na	2,5	65,31	23,0	0,97	39,36	25,95	6	0,254	**2,3**	0,2
	12	Mg	2,31	50,85	24,3	1,74	23,19	27,66	34	0,394	**18,4**	1,6
	13	Al	2,28	49,54	27,0	2,69	16,66	32,88	78	0,360	**51,5**	5,1
	14	Si				2,33	20,00		100	0,637		
	15	P				1,82	28,24		30	0,484		
	16	S				2,07	25,71		9	0,566		
	17	Cl										
	18	Ar										
4	19	K	2,91	101,9	39,1	0,86	75,47	26,47	3,4	0,229	**0,9**	0,07
	20	Ca	2,79	90,77	40,1	1,55	42,92	47,85	18	0,424	**9,5**	1,4
	21	Cs	2,67	79,56	44,9	2,99	24,95	54,82	44	0,765	**30,4**	5,1
	22	Ti	2,57	70,95	47,8	4,54	17,51	53,44	109	1,144	**81,7**	13,5
	23	V	2,49	64,53	50,9	6,11	13,84	52,69	139	1,512	**112,6**	18,2
	24	Cr	2,42	59,24	52,0	7,18	12,02	47,22	190	1,744	**150,1**	18,8
	25	Mn	2,36	54,94	54,9	7,21	12,65	42,29	123	1,798	**93,5**	12,7
	26	Fe	2,29	50,19	55,8	7,87	11,77	38,42	168	2,010	**127,7**	15,1
	27	Co	2,24	46,98	58,9	8,9	10,99	35,99	191	2,235	**145,1**	17,0
	28	Ni	2,18	43,30	58,7	8,9	10,85	32,45	186	2,348	**139,0**	13,8
	29	Cu	2,10	38.71	63,5	8,96	11,77	26,94	151	2,242	**104,2**	8,7
	30	Zn	2,10	38,71	65,4	7,13	15,29	23,42	79	1,785	**47,8**	3,4
	31	Ga	2,24	46,98	69,7	5,91	19,58	30,4	57	1,440	**36,8**	3,4
	32	Ge				5,32	22,65		77	1,285		
	33	As				5,73	21,70		39	1,383		
	34	Se				4,79	27,36		8	1,129		
	35	Br				3,12	42,51			0,749		
	36	Kr										
5	37	Rb	3,04	117,4	85,5	1,53	92,73	24,70	2,6	0,303	**0,55**	0,04
	38	Sr	2,99	111,7	87,6	2,54	57,26	54,47	12	0,603	**5,76**	0,9
	39	Y	2,83	94,74	88,9	4,47	33,01	61,73	45	1,075	**29,25**	5,5
	40	Zr	2,72	84,12	91,2	6,65	22,77	61,33	103	1,598	**75,2**	14,3
	41	Nb	2,63	76,04	92,9	8,57	17,99	58,05	170	2,072	**129,2**	23,3
	42	Mo	2,56	70,13	95,9	10,28	15,49	54,64	272	2,466	**209**	35,2
	43	Tc	2,50	65,31	98.	11,50	14,00	51,31	320	2,795	**249,6**	39,0
	44	Ru	2,44		101,1	12,37	13,56		270	2,952		
	45	Rh	2,39	57,06	102,9	12,45	13,72	43,34	180	2,989	**136,8**	18,1
	46	Pd	2,34	53,55	106,4	12,02	14,69	38,86	121	2,84	**88,3**	10,4
	47	Ag	2,30	50,85	107,8	10,49	17,07	33,78	45	2,50	**29,7**	3,1
	48	Cd	2,27	48,89	112,4	8,65	21.57	27,32	39	2,022	**21,5**	1,8
	49	In	2,41	58,50	114,8	7,31	26,07	32,43	55	1,71	**30,2**	3,3
	50	Sn	2,31	51,55	118,7	7,31	26,95	24,60	38	1,69	**17,8**	1,,2
	51	Sb	2,17	43,30	121,7	6,69	30,21	13,09	18	1,539	**5,4**	0,2
	52	Te				6,24	33,94		8	1,394		

The results of calculations are given in Table 10.2. For the calculations are used the maximum values R_0, given in the work [231]. The densities of elements, atomic mass are taken from [233, 236,237], the values of the elastic bulk modulus are taken from [234-235], stresses are calculated by formula (10.7).

The elastic deformation energy of atom is shown in tabl.10.2 too. Approximate estimations of this energy were made by formula $U_d = \int \sigma \cdot dV \approx \frac{1}{2}\sigma \Delta V$.

Estimations show that the stored energy of elastic deformation in the atom is very great and must be considered with a study of effects in solids.

2. Estimations of stresses from the data of volume change during the melting

Internal stresses can be also estimated, using data [234, 233] with respect to a change in the volume of material during the melting (see table 10.3). Latent heat of melting λ can be considered as energy of deformation (energy of increase of lattice parameters) per unit mass, i.e., as the energy, spent on an increase in the volume of the body at constant temperature of melting. Hence it is possible to find the stress

$$\sigma = \frac{\Delta E}{\Delta V} = \frac{m\lambda}{\Delta V} = \frac{\rho V \lambda}{\Delta V}, GPa \qquad (10.8)$$

Estimation according to (10.8) shows that inner stress reach to 4 – 22 GPa subject to element.

Table 10.3.

Period	Z	element	$\Delta V/V_t$ %	λ, кj/кg	ρ, 10^3 kg/m^3	σ, GPa	K, GPa
3	11	Na	2,2	115	0,96	4,1	6
	12	Mg	4,2	344	1,74	14,2	34
	13	Al	6,6	400	2,7	16,4	78
4	19	K	2,4	59,7	0,86	2,2	3,4
	30	Zn	6,9	102	6,9	10,2	70
5	47	Ag	5,0	105	10,5	22,0	45
	50	Sn	2,6	60	7,3	16,8	55
6	79	Au	5,2	60	19,3	22,3	170
	82	Pb	3,6	25	11,3	7,8	42

3. Estimations of stresses according to the data of the work [181]

For the results shown on fig.8.7, the identical value of conductivity testifies about the identical structure of material determined by internal stresses. Pressure of 0.1 GPa gives the same contribution to the solid's stress state as the temperature rise of 6,3 K, or the magnetic field H = 2.3 kΘ. So heating by Δ T ~ 300 K correspond to stresses Δσ ~ 4 GPa.

We see that different ways of estimation gives the same order of values. The greatest stresses 1- of 150 GPa are obtained during the estimation by Hooke's law, but this connected with the fact that we used data for the maximum values of the orbital radius of free atom.

So, **the total inner stress** consists of two components: the 'zero' stress already presented in solid before external influences and the stress created by the external influence. The second component can be managed in various ways: by the change of pressure, temperature, magnetic field in compliance with the eq. (10.5).

10.4. Nature of structural phase transformations

Phase transitions, observed in many materials, are fixed with respect to an abrupt change in their properties and are connected first of all with reconstruction of the structure of crystals. In accordance with the general principles of physics of crystals [238], reconstruction of structure occurs, when in the specific systems of deformation (slip, chipping, twinning, martensite transformation and others) are attained the critical values of the shear stresses of τ_c, which are the constant of material, which depends on the symmetry of lattice and elastic properties.

The concept of existence of the spectrum of the critical stresses (and, correspondingly, the spectrum of the critical or quantum values of energies) represents on the macrolevel the existence of the quantum energy states of the deformed atom in the solid. The specific critical form and volume of atom corresponds to each such quantum state of energy on the microlevel.

On the macrolevel the external influence (pressure, temperature and magnetic field) causes a linear change of the properties between the critical points, and the jump of properties upon transfer through these critical points. On the microlevel there is the linear (elastic) change for volume and form of atom under P, T and H impact between the critical points and the jump of the form and the size of atom upon transfer of the critical values of energy. The new adjustment of atoms to each other leads to a change in the symmetry of the crystal.

Note that for s- and p- elements, for which the distance between energy levels is sufficiently great, the significant energies are necessary for achievement critical volume; therefore the linear laws of volume elasticity and other properties acts over a wide range temperatures, pressures, magnetic field. For 3d, 4d- elements, in which the overlap of electron levels is observed, the several sequential structural transformations can be observed already in the small interval of the values of temperature, pressure, and field.

As it was said above, the tensor of the total internal stresses of σ_{ij} is a sum of the external stresses, caused by the action of temperature, pressure, magnetic field, and the internal "zero" stresses, relative to the deformation of electron shells at aggregation of atoms into solid. This stress tensor contains the diagonal components corresponded to volume change and the deviator part corresponded to shape part.

The main contribution to the tensor of total stresses give internal stresses, but with the aid of the action of one or several external factors (temperature, pressure, magnetic field) it is possible to substantially change the form of the tensor of total stresses in such a way that the critical value of stress will be achieved in the operational deformation systems and the structure of material will be reconstructed.

Shear stress is located as the convolution of the tensor of total stresses in the weakest and vulnerable direction in the anisotropic crystal:

$$\tau = \sigma_{ij} p_i q_j \tag{10.9}$$

where p_i, q_j are vector components that determine the surface and direction of the deformation systems, and σ_{ij} is tensor of total stresses.

Each of the parameters P, T, H gives the own contribution to value τ, as a result of cross effects (eq. 10.5). Because of the linearity (elasticity) of the contribution of thermo-, baro- and magnetoelastic components to the total stress the critical stress can be presented in the form to two-dimensional surface (3-axed ellipsoid) in 3-diomentions phase space, where along the axes are plotted the thermo-, baro- and magnet elastic components of stress (fig.10.7a). Actually this indicating surface of critical stresses is the phase diagram of the structural state of crystal.

Fig.10.7b shows the lines of level (isobar) which corresponds to section of surfaces of critical stresses at constant pressures when $P_3 > P_2 > P_1$. It should be noted that T - H - P diagram for the phase transitions in the ferroelectrics [1] and in perovskites [177] take the similar form, which testifies in favor proposed model.

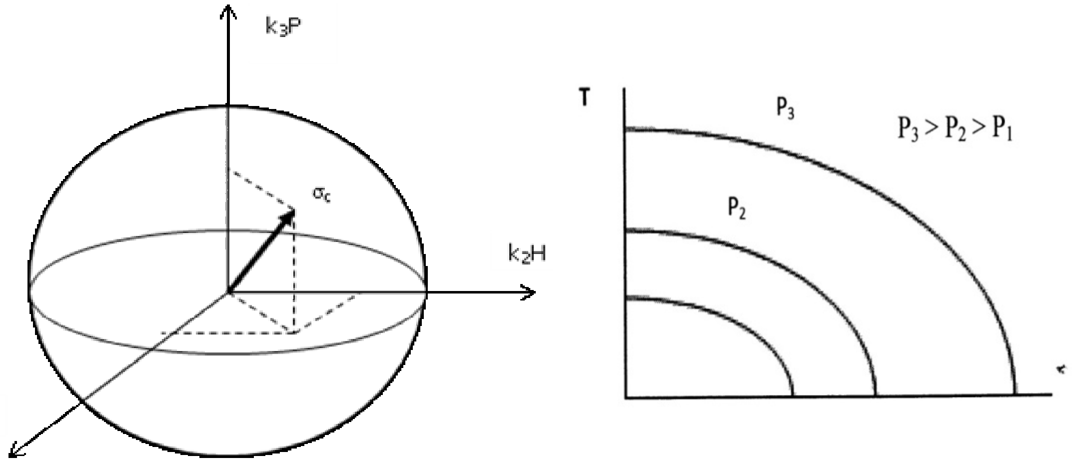


Figure 10.7. Surface of critical stresses (a) and level line (b) in the phase space (P, H, T).

The analysis of numerous studies of other materials (see previous chapters) shows that many anomalies and peculiarities of properties find the explanation within the frame of the suggested hypothesis. Internal stresses always be present in the material and indicate united nature of phase transitions as the consequence of a change in the structural symmetry of the crystals

Conclusions

1. Experiments under high pressure have shown the importance and the necessity of consideration of mechanical stresses in solids. Internal stresses are inalienable descriptions of new co-operative property of material found at the union of single atoms to a solid. Among other thermodynamic factors, stress can be considered as important integrating characteristics of a solid, as it is the most sensible to the material structure.
2. The appearance of internal stresses is conditioned by deformation of electron orbitals at the formation of a solid and depends on the nature of bonds between atoms. The anisotropic character of stresses is related to the anisotropic form and size of orbitals.
3. The value of stresses in solid is high (few GPa) and corresponded energy of elastic deformation of the atom too (few eV) therefore this stored elastic energy must be taken into account while considering many different effects.
4. Phase transitions are consequences of structural reconstructions of crystal at some critical stresses.
5. Influence of different external forces (temperature, magnetic field, pressures and oth.) causes change of internal stresses, because of cross effects. Therefore achievement of critical stresses in a crystal (and subsequent phase transition) can be achieved by different ways.

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