The Results of the Recalculation of the Effective X-ray Characteristic Temperature into Its Actual Value

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The paper discusses the results of the recalculation of the effective X-ray characteristic temperature $\Theta_{r.ef}$ obtained with corrections for thermal diffuse X-ray scattering, but without corrections for RMS static displacements of atoms in the crystal lattice from their equilibrium position, into an actual value $\Theta_{r.d}$, taking into account corrections for RMS dynamic and static displacements of atoms. The objects of investigation were disordered continuous solid solutions (alloys) of Cu-Ni, Au-Ag, Fe-Ni, KCl-KBr systems in the temperature range from room temperature to 300-600-700-800 °C. The methodology of finding the RMS general, dynamic and static values of the displacements of atoms from the equilibrium position and the method of recalculating $\Theta_{r.ef}$ into $\Theta_{r.d}$ are described. The research results are partly presented graphically and tabularly. Studies have shown that at room temperature the difference between $\Theta_{r.ef}$ and $\Theta_{r.d}$ for different alloys ranges from 4 to 28 K. At high temperatures, this difference drops to almost zero. The rate of decrease of $\Theta_{r.d}$ is greater than $\Theta_{r.ef}$, which is caused by taking into account the temperature concentration change of static displacements of atoms. The magnitude of the generalized measure of anharmonicity calculated from the temperature change $\Theta_{r.d}(T)$ is higher than $\Theta_{r.ef}(T)$. In addition, the rate of temperature change of the degree of anharmonicity calculated by $\Theta_{r.d}(T)$ is higher than that calculated by $\Theta_{r.ef}(T)$ both in magnitude and in the nature of change.

Keywords: X-ray, Characteristic temperature, Anharmonicity, Oscillations, Alloys.

1. INTRODUCTION

By physical content, the characteristic Debye temperature Θ conditionally divides the temperature limit of the quantum (at low temperatures) and classical (at high temperatures) description of oscillations of atoms of crystalline substances. There are other, even mathematical, definitions of the essence of Θ. Despite the blurring of the essence of Θ and some suggestions to avoid relying on this quantity, however, there are areas in physics where it is convenient to use Θ, even regardless of the way it is defined. In particular, it is a description of the anharmonicity of thermal oscillations of atoms in a crystal lattice. Especially this concerns the determination of the magnitude of the generalized degree of anharmonic oscillations of atoms $d\ln\Theta/dT$, where it is important to know not so much the Θ value as its change with a change in thermodynamic temperature.

When studying the dynamics of thermal oscillations of atoms in a crystal lattice, the behavior of the mean squares of the general $\overline{U_{gen}^2}$, dynamic $\overline{U_{dyn}^2}$ and static $\overline{U_{st}^2}$ displacements of atoms from the equilibrium position is studied. These shifts have an influence on the methods for determining the values of Θ in different ways (heat-intensive, elastic, X-ray, and other methods). Therefore, the values of Θ are slightly different.

In our opinion, the most experimentally simple, though mathematically more complex, is the X-ray method. X-rays react to any displacement of atoms.

This method in the first approximation determines the effective X-ray characteristic temperature $\Theta_{r.ef}$, taking into account corrections for thermal diffuse scattering (TDS) of X-rays [1, 2], which should be introduced into the real value of $\Theta_{r.d}$, taking into account corrections for the mean square of the static displacements $\overline{U_{st}^2}$.

2. DESCRIPTION OF OBJECTS AND METHODS OF RESEARCH

Based on the results of high-temperature X-ray investigations of disordered solid solutions (alloys) of Cu-Ni, Au-Ag, Fe-Ni, KCl-KBr systems described in the article [3], we calculated the values of $\Theta_{r.d}$ and $d\ln\Theta_{r.d}/dT$. We will remind, the essence of the high-temperature X-ray method of research consists in the analysis of temperature change in the integral intensity of the interference maximum of a certain index (*hkl*) and change in its position. According to the generally accepted Chipman-Paskin method [1, 2], the effective X-ray characteristic temperature and its temperature dependence $\Theta_{r.ef}(T)$, taking into account corrections for TDS, were found. The value of $\Theta_{r.ef}(T)$ determines the mean square of the general displacement $\overline{U_{gen}^2}$ of atoms from the equilibrium position in the lattice.

From an analysis of the temperature change in the crystal lattice period $a(T)$ of a solvent and a solid solution of a certain concentration, the mean square of the static displacement $\overline{U_{st}^2}$ of a hypothetical atom in the lattice was found. Since

$$\overline{U_{gen}^2} = \overline{U_{dyn}^2} + \overline{U_{st}^2}, \tag{1}$$

then

$$\overline{U_{dyn}^2} = \overline{U_{gen}^2} - \overline{U_{st}^2}. \tag{2}$$

The actual value of $\Theta_{r.d}$ was calculated from the $\overline{U_{gen}^2}$ values according to the formula

$$\Theta_{r.d.} = \sqrt{\frac{9hT\Psi(x)}{4\pi mk\overline{U_{dyn}^2}}}, \tag{3}$$

where $x\dfrac{\theta_{r.d}}{T}$, h is the Planck constant, k is the Boltzmann constant, T is the thermodynamic temperature on the Kelvin scale, m is the consolidated mass of a hypothetical atom in the alloy, $\Psi(x)$ is the Debye function, which with a high degree of accuracy from the tabular values of the Debye function and the set of values Θ/T is equal to

$$\Psi(x) = 1 + \alpha\frac{\theta^2}{T^2}, \tag{4}$$

where $\alpha = 0.0267$.

Representing the temperature dependences $\Theta_{r.ef}(T)$ and $\Theta_{r.d}(T)$ graphically and analytically in the form of typical dependences

$$\theta_{r.d}(T) = \theta_{p.273\,K} - b_1(T - 273), \tag{5}$$

$$\theta_{r.ef}(T) = \theta_{p.273\,K} - b_2(T - 273) \tag{6}$$

and determining the values of the coefficients b_1, b_2, after logarithmic differentiation of (5) and (6), we find a generalized measure of anharmonic oscillations of hypothetical alloy atoms by the ratios:

$$\frac{d\ln\theta_{r.d}}{dT} = \frac{-b_1}{\theta_{r.d\_temp.\_}}, \tag{7}$$

$$\frac{d\ln\theta_{r.ef}}{dT} = \frac{-b_2}{\theta_{r.ef\_temp.\_}} \tag{8}$$

at a given temperature T, K or t, °C.

3. DESCRIPTION AND ANALYSIS OF RESEARCH RESULTS

In the investigated temperature range, the values of the mean squares of static displacements of atoms from their equilibrium position in Au-Ag alloys lie within the experimental error [3]. Therefore, $\Theta_{r.ef}$, $\Theta_{r.d}$ and their universal measures of anharmonicity $d\ln\Theta_{r.ef}/dT$, $d\ln\Theta_{r.d}/dT$ practically coincide with each other (Fig. 1).

For other investigated alloys, the values of $\overline{U_{st}^2}$ are clearly visible and depend on both the concentration of the alloy content and the temperature. Therefore, the values of $\Theta_{r.ef}(T)$ and $\Theta_{r.d}(T)$ for a certain selected alloy are different at moderate temperatures, at high temperatures the difference between them goes to zero (Fig. 1, Table 1). Their temperature dependence, as a rule, is linear.

For all alloys in the investigated temperature range, $\Theta_{r.d}(T)$ is higher than $\Theta_{r.ef}(T)$. The generalized measures of anharmonicity $d\ln\Theta_{r.ef}/dT$ and $d\ln\Theta_{r.d}/dT$ calculated from the temperature change $\Theta_{r.d}(T)$ are higher in absolute value than those calculated from $\Theta_{r.ef}(T)$ (Fig. 2).
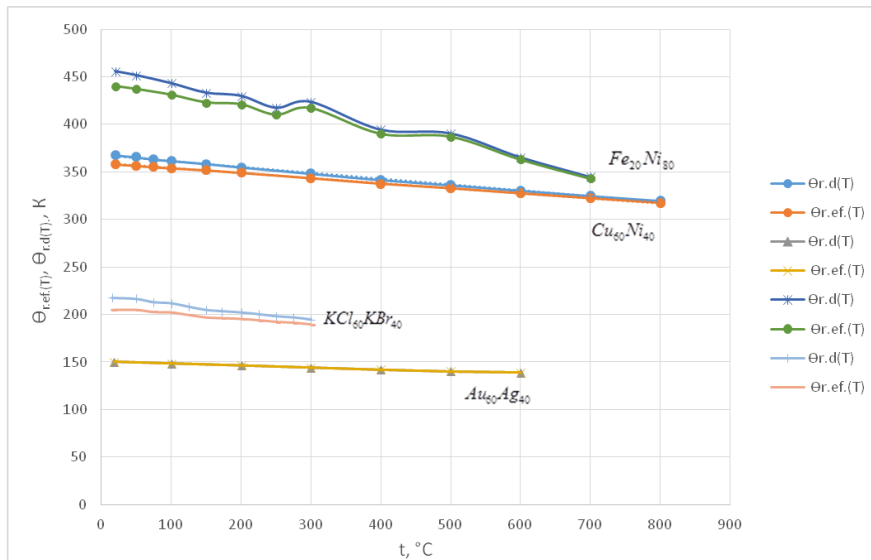

Fig. 1 – Comparative temperature dependences of $\Theta_{r.d}$ and $\Theta_{r.ef}$ of the investigated alloys

Table 1 – Values of temperature dependences of $\Theta_{r.ef}$, $\Theta_{r.d}$, $d\ln\Theta_{r.ef}/dT$, $d\ln\Theta_{r.d}/dT$ of the selected investigated alloys

Alloy composition	t, °C	T, K	$\Theta_{r.ef}$, K	$\Theta_{r.d}$, K	$\left|-\dfrac{d\ln\theta_{r.ef}}{dT},10^{-4}\dfrac{1}{K}\right|$	$\left|-\dfrac{d\ln\theta_{r.d}}{dT},10^{-4}\dfrac{1}{K}\right|$
Cu$_{60}$Ni$_{40}$	20	293	358.0	367.6	1.688	1.476
	200	473	349.1	354.9	1.748	1.513
	400	673	337.6	341.6	1.816	1.565
	600	873	327.4	330.3	1.878	1.614
	800	1073	317.3	319.6	1.941	1.665
Au$_{60}$Ag$_{40}$	18	291	150	150.0	1.310	1.310
	200	473	146.2	146.2	1.344	1.344
	400	673	141.8	141.8	1.386	1.386
	600	873	139	139.0	1.414	1.414
Fe$_{50}$Ni$_{50}$	20	293	440	468.3	2.381	1.813
	200	473	426	442.3	2.520	1.872
	400	673	408	417.9	2.668	1.955
	600	873	394	400.8	2.781	2.025
KCl$_{60}$KBr$_{40}$	15	288	205	217.7	3.922	2.861
	100	373	202.3	212.0	4.029	2.900
	200	473	195.3	202.0	4.227	3.004
	300	573	189.3	194.4	4.393	3.099

Note: the composition of metal alloys is given in atomic percent, and of ionic alloys – in mole percent
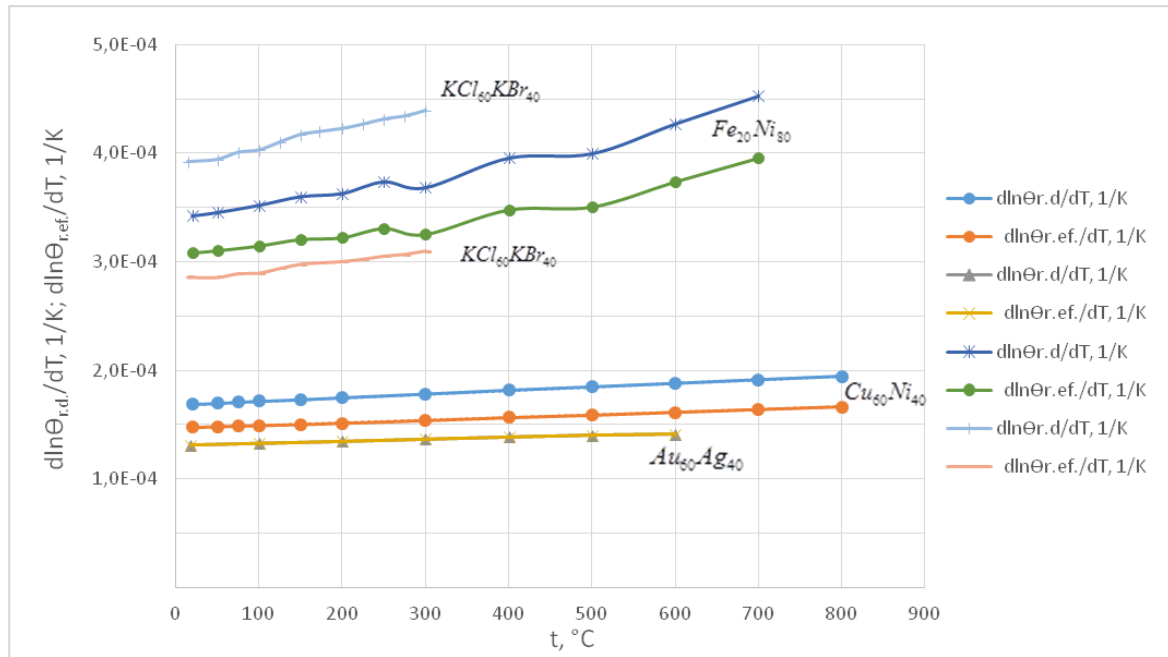

Fig. 2 – Comparative temperature dependences of $d\ln\Theta_{r.ef}/dT$ and $d\ln\Theta_{r.d}/dT$ of the investigated alloys

A characteristic feature of the investigated alloys, in addition to Au-Ag, is that with increasing impurities in solvents, the difference between $\Theta_{r.d}$ and $\Theta_{r.ef}$ also increases. At room temperature it is 4-5 K and at an impurity concentration of 50 % it reaches 10-12 K. The largest difference between the values of $\Theta_{r.d}$ and $\Theta_{r.ef}$ is in Fe-Ni alloys, it increases from 6-12 K to 28 K at an impurity concentration of 50 at. % caused by a significant RMS static displacement of hypothetical atoms of the crystal lattice (Table 2).

For all Au-Ag alloys, due to the paucity of values $\overline{U_{st}^2}$ the difference between $\Theta_{r.d}$ and $\Theta_{r.ef}$ is almost 0 K.

Table 2 – Difference between $\Theta_{r.d}$ and $\Theta_{r.ef}$ values for alloys at room temperature

Alloy	$\Delta\Theta$, K	Alloy	$\Delta\Theta$, K	Alloy	$\Delta\Theta$, K
Cu$_{90}$Ni$_{10}$	4	Fe$_{65}$Ni$_{35}$	12	KCl$_{90}$KBr$_{10}$	5
Cu$_{80}$Ni$_{20}$	7	Fe$_{56}$Ni$_{44}$	28	KCl$_{80}$KBr$_{20}$	8
Cu$_{70}$Ni$_{30}$	9	Fe$_{50}$Ni$_{50}$	28	KCl$_{70}$KBr$_{30}$	10
Cu$_{60}$Ni$_{40}$	10	Fe$_{30}$Ni$_{70}$	19	KCl$_{60}$KBr$_{40}$	10
Cu$_{50}$Ni$_{50}$	10	Fe$_{27}$Ni$_{73}$	17	KCl$_{50}$KBr$_{50}$	12
Cu$_{40}$Ni$_{60}$	7	Fe$_{20}$Ni$_{80}$	16	KCl$_{40}$KBr$_{60}$	11
Cu$_{30}$Ni$_{70}$	5	Fe$_{10}$Ni$_{90}$	6	KCl$_{30}$KBr$_{70}$	8
Cu$_{20}$Ni$_{80}$	5			KCl$_{10}$KBr$_{90}$	3
Cu$_{10}$Ni$_{90}$	3				

With increasing temperature, the rate of decline of $\Theta_{r.d}(T)$ is greater than the rate of decline of $\Theta_{r.ef}(T)$ (Fig. 1), and this leads to different values of the generalized measures of anharmonic oscillations of atoms (($d\ln\Theta_{r.ef}/dT)(T)$ and ($d\ln\Theta_{r.d}/dT)(T)$).

A measure of impetuosity of temperature change of $\Theta_{r.ef}(T)$ and $\Theta_{r.d}(T)$ (respectively, ($d\ln\Theta_{r.ef}/dT)(T)$ and ($d\ln\Theta_{r.d}/dT)(T)$), can be the coefficient of proportionality of their analytical dependences. For example, for selected alloys, they are shown in Table 3.

Table 3 – Analytical dependences of temperature change of the above values for alloy samples

Analytical dependence	Alloy
$\Theta_{r.d}(t) = 383.2 - 6.0066 \cdot 10^{-2}t$	$Cu_{40}Ni_{60}$
$\Theta_{r.ef}(t) = 376.3 - 5.3200 \cdot 10^{-2}t$	$Cu_{40}Ni_{60}$
$\Theta_{r.d}(t) = \Theta_{r.ef}(t) = 148.0 - 5.4687 \cdot 10^{-2}t$	$Au_{40}Ag_{60}$
$\Theta_{r.d}(t) = 441.7 - 1.4883 \cdot 10^{-1}t$	$Fe_{30}Ni_{70}$
$\Theta_{r.ef}(t) = 424.8 - 1.24883 \cdot 10^{-1}t$	$Fe_{30}Ni_{70}$
$\Theta_{r.d}(t) = 204.3 - 8.8604 \cdot 10^{-2}t$	$KCl_{40}KBr_{60}$
$\Theta_{r.ef}(t) = 194.4 - 6.6227 \cdot 10^{-2}t$	$KCl_{40}KBr_{60}$
$(d\ln\Theta_{r.d}/dT)(t) = = 0.1665 \cdot 10^{-3} + 3.1867 \cdot 10^{-8}t$	$Cu_{50}Ni_{50}$
$(d\ln\Theta_{r.ef}/dT)(t) = 0.1446 \cdot 10^{-3} + 2.3626 \cdot 10^{-8}t$	$Cu_{50}Ni_{50}$
$d\ln\Theta_{r.ef}/dT)(t) = (d\ln\Theta_{r.d}/dT)(t) = = 0.1307 \cdot 10^{-3} + 1.8558 \cdot 10^{-8}t$	$Au_{60}Ag_{40}$
$\ln\Theta_{r.d}/dT)(t) = 0.2377 \cdot 10^{-3} + 6.7347 \cdot 10^{-8}t$	$Fe_{50}Ni_{50}$
$(d\ln\Theta_{r.ef}/dT)(t) = 0.1799 \cdot 10^{-3} + 3.7019 \cdot 10^{-8}t$	$Fe_{50}Ni_{50}$
$(d\ln\Theta_{r.ef}/dT)(t) = 0.4170 \cdot 10^{-3} + 2.0037 \cdot 107t$	$KCl_{50}KBr_{50}$
$(d\ln\Theta_{r.d}/dT)(t) = 0.3052 \cdot 10^{-3} + 1.0331 \cdot 10^{-7}t$	$KCl_{50}KBr_{50}$

Quantities $d\ln\Theta/dT$ are given in absolute values.

With increasing temperature, the difference between $\Theta_{r.d}(T)$ and $\Theta_{r.ef}(T)$ for most alloys decreases almost to zero. The generalized measure of anharmonicity calculated from the temperature change $\Theta_{r.d}(T)$ is higher than that calculated from $\Theta_{r.ef}(T)$. In addition,

the rate of temperature change in the measure of anharmonicity calculated for $\Theta_{r.d}(T)$ is higher than that calculated for $\Theta_{r.ef}(T)$. As expected, KCl-KBr alloys are the most anharmonic, Fe-Ni – less, Au-Ag – the least.

4. CONCLUSIONS

The recalculation of $\Theta_{r.ef}$ into the actual value $\Theta_{r.d}$ with corrections for the change in RMS static displacements of atoms showed that in the investigated temperature range at room temperature, the values of $\Theta_{r.d}$ are greater than $\Theta_{r.ef}$ for solid solutions (alloys) of Cu-Ni, KCl-KBr systems by 4-5 K, and at an impurity concentration of 50 at. % in the solvent the difference between $\Theta_{r.d}$ and $\Theta_{r.ef}$ reaches 10-12 K. Only at high temperatures this difference goes to zero. The largest difference between $\Theta_{r.d}$ and $\Theta_{r.ef}$ in solid solutions of Fe-Ni at room temperature reaches 6-12 K, and at an impurity concentration of 50 at. % it increases to 28 K. This is due to a significant change in $\overline{U_{st}^2}$. Only for Au-Ag alloys due to ultra-small $\overline{U_{st}^2}$ this difference is almost zero. The temperature rate of decrease of both characteristic temperatures with increasing T is greater in $\Theta_{r.d}$. This leads to different values of generalized measures of anharmonicity ($d\ln\Theta_{r.d}/dT)(T)$ and ($d\ln\Theta_{r.ef}/dT)(T)$ of oscillations of atoms in the crystal lattice of the investigated solid solutions, except for Au-Ag alloys. Therefore, in the case of using anharmonic measures, when calculating the values of measures of anharmonicity, corrections for temperature and concentration changes in the values of $\overline{U_{st}^2}$ should be taken into account.

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Результати перерахунку ефективної рентгенівської характеристичної температури в її дійсне значення

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У статті обговорюються результати перерахунку ефективної рентгенівської характеристичної температури $\Theta_{r.ef}$, одержаної з поправками на теплове дифузне розсіювання рентгенівських променів, але без поправок на середньоквадратичні статичні зміщення атомів у кристалічній ґратці від їх положення рівноваги, у дійсне значення з урахуванням поправок на середньоквадратичні динамічні та статичні зміщення атомів. Об'єктами досліджень були неупорядковані безперервні тверді розчини (сплави) систем Cu-Ni, Au-Ag, Fe-Ni, KCl-KBr в інтервалі температур від кімнатних до 300, 600, 700 і 800 °C. Описана методика знаходження середньоквадратичних загальних, статичних і динамічних значень зміщень атомів від положення рівноваги та методика перерахунку $\Theta_{r.ef}$ в $\Theta_{r.d}$ сплавів. Результати досліджень частково представлені графічно і таблично. Дослідження показали, що при кімнатній температурі різниця між $\Theta_{r.ef}$ і $\Theta_{r.d}$ для різних сплавів сягає від 4 до 28 К. При високих температурах ця різниця спадає майже до нуля. Стрімкість зменшення $\Theta_{r.d}$ більша за $\Theta_{r.ef}$, що спричинено врахуванням

температурної концентраційної зміни статичного зміщення атомів. За величиною, узагальнююча міра ангармонізму, що розрахована за температурною зміною $\Theta_{r.d}(T)$, вища за $\Theta_{r.ef}(T)$. Крім того, стрімкість температурної зміни міри ангармонізму, розрахована за $\Theta_{r.d}(T)$, вища розрахованої за $\Theta_{r.ef}(T)$ як за величиною, так і за характером зміни.