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The Grüneisen Parameter and the Apparent Part of the General Measure of Anharmonicity of Solid Solutions of the Fe-Ni System

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The temperature and concentration dependences of the nanometric parameter of crystal lattice of Fe-Ni alloys in the range of 293-973 K were studied with the high-temperature X-ray diffraction method using the "CROS"-type camera. The change of the Debye's X-ray characteristic temperature, the general measure of anharmonicity, it's implicit and explicit parts, the Grüneisen parameter were investigated. The discrepancy between the individual values and the mean values of the Grüneisen parameter was explained. One part of the research results was presented analytically and the other was presented graphically. The nature of temperature and concentration changes correlate with each other. It was investigated that for invar alloys (35-35.6 at. % Ni) the linear expansion coefficient is small, and for super invar alloys (42-48 at. % Ni) the coefficient of linear expansion is almost constant in the range of 273-573 K. In connection with these features, it was foreseen to estimate the value of the explicit part of anharmonicity measure, due to the growth of sample temperature. The temperature dependence of the lattice constant and the logarithm of the relative integral intensity of diffraction peaks reflection were investigated at room temperature and at higher temperatures. By the Chipman's method, taking into account the correction on thermal diffusive scattering, the temperature dependence of the effective X-ray characteristic temperature was determined. It was investigated that the temperature dependence of the actual coefficient of linear expansion of permalloy alloys is similar in magnitude and character. For invar alloys it differs significantly in magnitude and in character from permalloy alloys. The prospect of using a high-temperature X-ray method for determining the Grüneisen parameter in studying the structure and interatomic bonds of ferromagnetic solids was substantiated.

Keywords: Grüneisen Parameter, X-ray, Anharmonism, Crystal lattice.

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1. INTRODUCTION

Iron-based alloys are important materials and widely used in various industries. For example, iron-based alloys are used as filtering nozzles for magnetic purification of liquid and gaseous media in many industrial plants [1]. This is especially goes for alloys of the Fe-Ni system, in particular, invar and permalloy alloys.

In the framework of nanoelectronic physics, the study of the characteristics of the thermal vibrations of crystal lattice atoms has a significant theoretical and practical importance. The study of the physical characteristics of the thermal vibrations of crystal lattice atoms by various methods makes it possible to generalize the behavior of these oscillations, to investigate the behavior of all new characteristics, for example, the temperature and concentration dependences of the Grüneisen parameter.

2. DESCRIPTION OF THE OBJECT AND RESEARCH METHODS

The studied materials were solid solutions (alloys) of the Fe-Ni system with 35, 44, 50, 70, 73, 80, 90, 100 atomic percentages of nickel in the alloy. The source materials were electrolytic nickel and granular iron.

Alloys were prepared in a high-frequency oven under excess pressure in an atmosphere of purified argon followed by slow cooling of the oven with ingots. Subsequently, the ingots were subjected to generally accepted mechanical and thermal actions, provided for the preparation of samples for X-ray analysis similar to the work [2]. Powder from such ingots was poured out in an agate mortar to produce fine-grained grains. The powder was pressed in the form of tablets in iron substrate capsules and burned off in a vacuum at a temperature of 1170 K for one hour with slow cooling in the oven.

Homogeneity and structure of samples were determined by metallographic and X-ray methods. The composition of alloys was controlled by chemical and spectral analyzes.

The criterion for the suitability of the samples for the study was a clear separation of doublets $K_{\alpha 1}$ and $K_{\alpha 2}$ on radiographs, lack of texture and obtaining continuous diffraction peaks without rotation of the sample and the pellicle.

High-temperature X-ray diffraction of each sample was carried out several times in the range of 293-973 K in an inert medium with increasing and decreasing temperature, then with the replacement of samples of the same composition and one production series. This made it possible to control the growth of the extinction effect due to the change in the metallographic grains at high temperatures.

A characteristic feature of invar alloys (35-35.6 at. % Ni) is their small linear expansion coefficient and of "super" invar alloys (42-48 at. % Ni) – their almost constant coefficient of linear expansion in the range of 273-573 K. In connection with these features, it was foreseen to estimate the value of the explicit part of the anharmonicity measure due to the growth of sample temperature.

High-temperature X-ray diffraction was carried out by a "CROS"-type camera with a high-temperature nozzle on iron K_α-irradiation. An analysis of the tem-

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perature dependence of the interference maximum (222) was carried out, taking into account the corrections for thermal diffusive scattering (TDS) of X-rays.

Using the special diagrams, we investigated the temperature dependence of lattice constant $a(T)$ and logarithm of the relative integral intensity of diffraction peaks reflection (222) at room temperature and at higher temperatures T. Reproducibility was high. The absolute error in determining the period of the crystal lattice was $\Delta a = \pm 0.0002$ Å. After analyzing different methods for determining the Debye's characteristic temperature, we preferred heat-intensive, elastic and X-ray methods. We chose the X-ray method among them.

By the Chipman's method [3], taking into account the correction on the TDS, the temperature dependence of the effective X-ray characteristic temperature $\Theta_R(T)$ was determined.

As known, the Grüneisen parameter γ is determined for monatomic substances by the ratio:

$$\gamma = -\frac{d\ln\theta_D}{d\ln V}, \quad (1)$$

where Θ_D is the Debay's characteristic temperature, V is the molar volume of matter.

Since the masses of Fe and Ni atoms differ slightly from each other, we can assume that the ratio (1) can be applied to alloys of the Fe-Ni system.

In addition, judging by the diagram of the state of the Fe-Ni system, in the temperature and concentration limits of the research the alloys have a face-centered cubic (FCC) lattice.

The values of Θ_D and Θ_R are close to each other, so using relation (1) we can found γ:

$$\ln\theta_R = -\gamma \ln V + const. \quad (2)$$

The experimental results show that the temperature dependence $\Theta_R(T)$ can be expressed by the ratio:

$$\theta_R(T) = \theta_{R\ 273\ K} - b(T - T_0) = \theta_{R\ 273\ K} - b(T - 273) = \theta_{R0^0C} - bt, \quad (3)$$

where b is the dimensionless coefficient of proportionality, T is the temperature on the Kelvin scale, t is the temperature on the Celsius scale.

It should be noted that the physical meaning of an effective X-ray characteristic temperature Θ_R is a bit unfocused. It can be regarded as the temperature from which all kinds of oscillatory motion of lattice atoms are beginning. However, not so much importance of Θ_R as its change with temperature is important.

In particular, from the equation (3) we can calculate the universal measure of the anharmonicity of the crystal lattice thermal vibrations:

$$\frac{d\ln\theta_R}{dT} = -\frac{b}{\theta_{R_i}}. \quad (4)$$

Since, based on thermodynamic considerations:

$$\frac{d\ln\theta_R}{dT} = -\gamma\beta + \frac{\partial\ln\theta_R}{\partial T}, \quad (5)$$

where $\gamma\beta$ (β is the real coefficient of volume expansion) is an implicit part of the universal measure of anharmonicity due to volume change; $\partial ln\Theta_R/\partial T$ is an obvious part, because of temperature change, then for invar alloys at insignificant temperatures you can find a clear part of anharmonicity.

Taking into account that the general measure of anharmonicity can be expressed in parts of $\gamma\beta$, so by the relation:

$$\frac{d\ln\theta_R}{dT} = -n\gamma\beta \quad (6)$$

you can follow the change in the magnitude of the dimensionless coefficient of proportionality n.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

According to the results of the research, the concentration dependence of the constant crystal lattice $a(c)$ of alloys is obtained, which is shown in Fig. 1.

The temperature dependence of the effective X-ray characteristic temperature for Fe-Ni alloys is expressed by ratios (temperature in Kelvin) shown in Table 1.

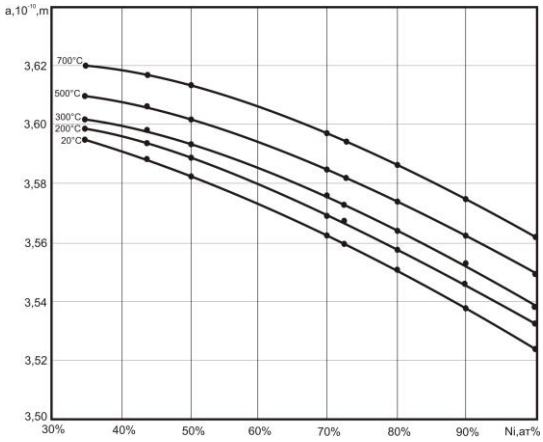

Fig. 1 – Concentration dependence of the crystal lattice parameter $a(c)$ of Fe-Ni alloys at different temperatures

Table 1 – Temperature dependence of the effective X-ray characteristic temperature for Fe-Ni alloys

$\Theta_p(t) = 381.42 - 0.0647t$	35 %
$\Theta_p(t) = 439.43 - 7.2438\cdot10^{-3}t - 4.0350\cdot10^{-5}t^2$	44 %
$\Theta_p(t) = 441.76 - 0.0784t$	50 %
$\Theta_p(t) = 421.06 - 0.1204t$	70 %
$\Theta_p(t) = 421.36 - 0.1462t$	73 %
$\Theta_p(t) = 445.21 - 0.1374t$	80 %
$\Theta_p(t) = 444.34 - 0.1623t$	90 %
$\Theta_p(t) = 422.99 - 0.0513t$	100 % *Ni*

The character of temperature dependences $a(c)$ and $\Theta_R(t)$ is explained by the anharmonicity of crystal lattice atoms thermal vibrations of Fe-Ni alloys. A characteristic feature of the concentration dependence of the crystal lattice parameter of the Fe-Ni system at different temperatures is its increase with increasing Fe amount in the alloy. This is due to the fact that $a_{Fe} > a_{Ni}$ (Fig. 1).

The nature of the temperature dependence of the actual coefficient of linear expansion $\alpha_D(t)$ of permalloy

alloys is similar in magnitude and character. For invar alloys (35; 44 at. % Ni) it differs significantly in magnitude and in character from permaloy alloys (50-90 at. % Ni) (Fig. 2).

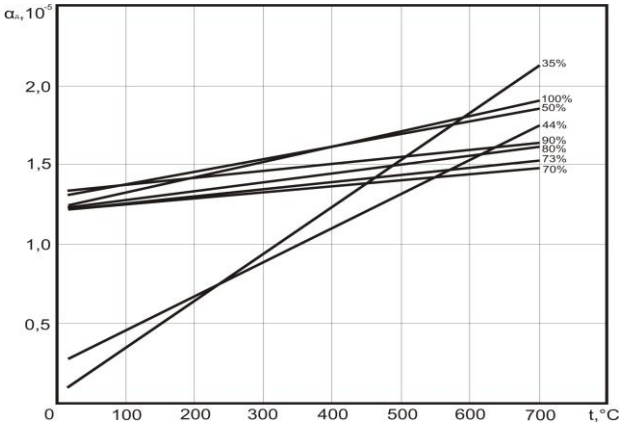

Fig. 2 – Temperature dependence of the actual coefficient of linear expansion $\alpha_D(t)$ of Fe-Ni system alloys

We explain this by peculiarities of the thermo- and magnetostrictive properties of alloys with 35 and 44 at. % of nickel in Fe-Ni alloys.

This dependence for the invar and super invar alloys is due not only to the influence of the anharmonicity of thermal vibrations of crystal lattice atoms, which is the only reason for the change in the size in the dia- and paramagnets. In ferromagnets, the change in temperature leads to a change in their magnetization and to magnetostriction. Therefore, the full real coefficient of thermal expansion of ferromagnetic materials consists of the component α_a due to the anharmonicity of the oscillations and the component α_m due to the magnetostriction:

$$\alpha = \alpha_a + \alpha_m . \qquad (7)$$

The first component is always positive, and the second component can be positive, equal to zero or negative. At a temperature of 293-323-573 K, invar and super invar alloys have a negative ferromagnetic component α_m. When the samples are heated to the Curie temperature, the normal component of the thermal expansion α_a is compensated by the decreasing component α_m, because the spontaneous magnetization decreases with temperature increasing.

The concentration dependence of the Debye's X-ray characteristic temperature $\Theta_R(c)$ at different temperatures of the alloys has a complex character and at low temperatures this dependence is smoother by character, and at high temperatures it has sagging character. This indicates that all modes of oscillatory motion in the Fe-Ni alloys are switched in different ways.

In the presence of the dependences $a(c)$, $\Theta_R(t)$ and the graph-analytic relation (2), the Grüneisen parameter γ is determined. Temperature change of the Grüneisen parameter of alloys was not observed. This testifies that in the investigated temperature interval the structure of the crystal lattice of alloys has not changed, and the concentration change of the Grüneisen parameter depends on the magnetic interaction of crystal lattice atoms (Fig. 3).

The temperature dependence of the general measure of anharmonicity $d\ln\Theta_R/dT$ of the investigated alloys increases by magnitude and decreases with the sign (Fig. 4). This dependence for the investigated alloys is similar.

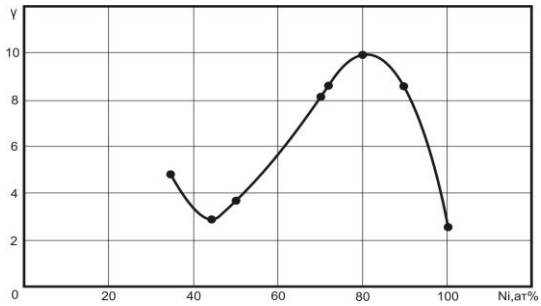

Fig. 3 – Concentration dependence of the Grüneisen parameter $\gamma(c)$ of the investigated Fe-Ni alloys

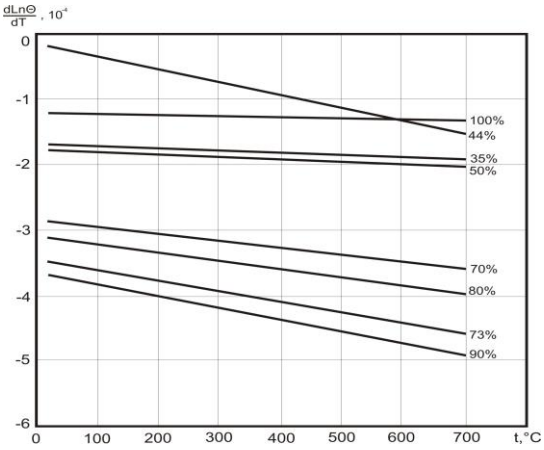

Fig. 4 – Temperature dependence of the general measure of anharmonicity of investigated Fe-Ni alloys

The presence of the values of the Grüneisen parameter γ and the volumetric thermal expansion coefficient of the lattice β made it possible to determine the implicit part of the general measure of anharmonicity $\gamma\beta(t)$ of investigated alloys which is shown in Fig. 5. The temperature growth of the general measure of anharmonicity $\gamma\beta(t)$ for invar alloys correlates with the behavior of $\alpha_D(t)$.

By relation (5) it was found the temperature change of the explicit part of the general measure of investigated alloys anharmonicity (Table 2).

From Fig. 4, Fig. 5 and Table 2 it can be seen that for an invar alloy with 35 at. % Ni, the values $d\ln\Theta_R/dT$ and $\partial\ln\Theta_R/\partial T$ are of the same order when heated to 200 ºC. This is due to the invariability of the thermal coefficient of the volumetric expansion of the crystal lattice in this temperature range. For other alloys, the value of $\partial\ln\Theta_R/\partial T$ is substantially smaller than $d\ln\Theta_R/dT$.

The results of the researches show that with the exception of the invar alloy the general measure of anharmonicity is essentially exhausted by the implicit part $\gamma\beta$ associated with the thermal expansion of the crystal lattice. Therefore, according to (6), the value of the dimensionless coefficient n for permalloy alloys is close to one, especially at high temperatures.

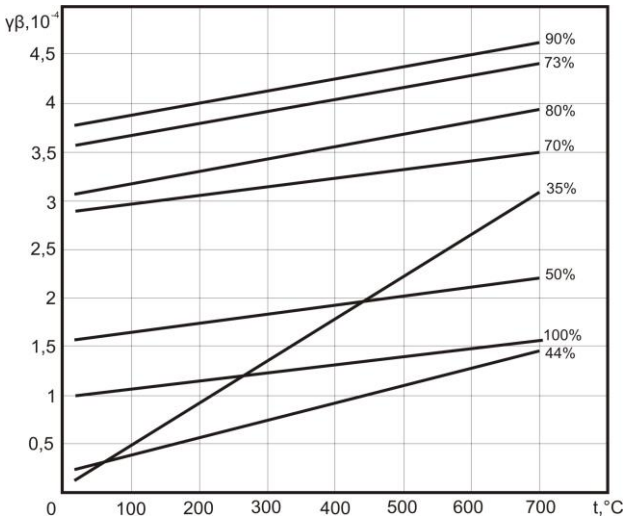

Fig. 5 – Temperature dependence of the implicit part of the general measure of anharmonicity of Fe-Ni alloys

4. CONCLUSIONS

The temperature dependences $a(c)$ and $\Theta_R(T)$ are determined by the method of high-temperature X-ray diffraction with the help of the "CROS"-type camera with high temperature nozzle.

On their basis, the Grüneisen parameter γ, the general measure of the anharmonicity $dln\Theta_R/dT$, the implicit $\gamma\beta$ and the explicit $\partial ln\Theta_R/\partial T$ parts of the general measure of Fe-Ni alloys anharmonicity are determined.

For an invar alloy containing 35 at. % Ni, an explicit part of the general measure of anharmonicity $\partial ln\Theta_R/\partial T$ is of the same order as $dln\Theta_R/dT$. For the remaining permalloy alloys $\partial ln\Theta_R/\partial T$ is substantially smaller than $dln\Theta_R/dT$.

The Grüneisen parameters γ for alloys are different, which indicates the difference in atomic bonds, although the crystal structure neither on temperature nor on the composition of the investigated ferromagnetic alloys has not changed.

For most alloys, the dimensionless parameter n is close to one, especially at high temperatures, which indicates the temperature rising of the $\gamma\beta$ value.

The high-temperature X-ray diffraction method of Grüneisen parameter γ, $dln\Theta_R/dT$, $\partial ln\Theta_R/\partial T$ definition has a perspective in the investigation of nanometric structure and interatomic bonds of alloys including ferromagnetic solids.

Table 2 – The value of an explicit part of the general measure of anharmonicity $\partial ln\Theta_R/\partial T$ of investigated alloys at different temperatures, 10^{-4} 1/K

t, °C	T, K	Fe-Ni alloys, at. % Ni							
		35	44	50	70	73	80	90	100
20	293	–1.56	0.032	–0.23	0.016	0.041	–0.06	0.083	–0.21
50	323	–0.44	0.031	–0.21	0.017	0.042	–0.05	0.08	–0.19
100	373	–1.24	0.029	–0.18	0.019	0.042	–0.03	0.07	–0.16
150	423	–1.04	0.027	–0.15	0.018	0.040	–0.02	0.06	–0.13
200	473	–0.83	0.023	–0.11	0.017	0.035	–0.008	0.04	–0.1
250	523	–1.63	0.019	–0.09	0.014	0.028	–0.003	0.002	–0.07
300	573	–0.43	0.013	–0.06	0.01	0.018	–0.014	0.01	–0.04
400	673	–0.34	0.004	–0.004	0.002	–0.01	0.028	–0.03	0.01
500	779	0.36	–0.016	0.05	–0.022	–0.05	0.033	–0.1	0.07
600	873	0.75	–0.037	0.1	–0.049	–0.1	0.029	–0.18	0.13
700	973	1.14	–0.062	0.16	–0.085	–0.18	0.014	–0.28	0.19

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Параметр Грюнайзена та явна частина узагальнюючої міри ангармонізму твердих розчинів системи Fe-Ni

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Високотемпературним рентгенографічним методом за допомогою камери КРОС досліджені температурна та концентраційна залежності нанометричного параметра кристалічної ґратки сплавів системи Fe-Ni в діапазоні 293-973 К. Досліджена зміна рентгенівської характеристичної температури Дебая, узагальнююча міра ангармонізму, її неявна та явна частини, параметр Грюнайзена. Пояснюються розбіжності значень окремих сплавів та середніх їх значень. Частина результатів дослідження представлена аналітично, а інша – графічно. Характер температурних і концентраційних змін корелюється між собою. Досліджено, що у інварних сплавів (35-35,6 ат. % Ni) коефіцієнт лінійного розширення є незначним, а у суперінварних сплавів (42-48 ат. % Ni) коефіцієнт лінійного розширення майже постійний в межах 273-5730 К. У зв'язку з такими особливостями передбачалась можливість оцінити величину явної частини міри ангармонізму, зумовлену зростанням температури зразка. За кросограмами досліджувались температурні залежності періоду кристалічної ґратки і логарифму відносної інтегральної інтенсивності дифракційних максимумів відбивання при кімнатній температурі та при вищих температурах. За методом Чіпмана з врахуванням поправки на теплове дифузне розсіювання визначалась температурна залежність ефективної рентгенівської характеристичної температури. Досліджено, що температурна залежність дійсного коефіцієнта лінійного розширення пермалойних сплавів зі значним вмістом Ni за величиною і характером подібна. Для інварних сплавів вона значно відрізняється і за величиною і за характером від пермалойних сплавів. Обґрунтована перспективна застосування високотемпературного рентгенівського методу визначення параметра Грюнайзена при вивченні структури та міжатомних зв'язків феромагнітних твердих тіл.

Ключові слова: Параметр Грюнайзена, Рентгенографія, Ангармонізм, Кристалічна ґратка.