

Structure sensitivity of parameters of acoustic relaxation α -peak in niobium and iron

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Influence of dislocation structure on parameters of low-temperature internal friction α -peak and related Young's modulus defect has been studied in niobium single crystals and polycrystals and pure iron single crystals. A statistical interpretation of the temperature dependence and structure sensitivity of dynamic relaxation characteristics in the vicinity of α -peak has been proposed based on assumed random scatter of activation energy of elementary relaxators. The attempt period, average value, and dispersion of activation energy have been estimated for the relaxation process responsible for the α -peak in the materials studied.

На моно- и поликристаллах ниобия с различной концентрацией примесей, а также на монокристаллах чистого железа экспериментально изучено влияние изменения дислокационной структуры образцов на параметры низкотемпературного α -пика внутреннего трения и соответствующего ему дефекта модуля Юнга. Предложена статистическая интерпретация температурной зависимости и структурной чувствительности характеристик динамической релаксации в окрестности α -пика, основанная на предположении о случайном разбросе значений энергии активации элементарных релаксаторов. Получены эмпирические оценки для периода попыток, среднего значения и дисперсии энергии активации релаксационного процесса, ответственного за α -пик в изученных материалах.

When studying temperature dependences of internal friction in niobium samples of different purity and structure perfection grades, various authors have observed in moderately low temperature region acoustic absorption peaks with properties typical of α -peaks in bcc metals. The peak localization temperature T_p varies from 90 K to 200 K as the vibration frequency varies within wide limits from infrasound values of about 10^{-3} Hz up to ultrasonic region of about 10^5 Hz [1–13].

The sample plastic pre-straining or the action of thermoelastic stresses during thermocycling result in increased height and width of the absorption peaks as well as in the T_p shift towards higher temperatures. The subsequent prolonged low-temperature annealing causes reverse changes of the absorption peak parameters. These behavior

peculiarities of the absorption peak shape and parameters evidence its sensitivity to defect structure details of the sample under study, in particular, to statistical dislocation ensemble and random fields of internal stresses caused thereby that are introduced into the crystal samples due to plastic deforming.

A similar relaxation resonance was observed also in studies of internal friction in high-purity iron. At vibration frequencies about 10^5 Hz, the acoustic relaxation peak is observed at temperatures about 50 K [14–21]. In contrast to niobium, α -peak in iron is observed in plastic-deformed samples. It is to note that the low-temperature absorption peak was observed also when the internal friction in pure iron was studied using low-frequency methods. At vibration frequency about 1 Hz, this peak was re-

Table 1

Sample	Structure	c , p.c. (at.)
Nb-37	Single crystal $\langle 100 \rangle$	$8.0 \cdot 10^{-2}$
Nb-60	Polycrystal (grain 0.1 mm)	$5.0 \cdot 10^{-2}$
Nb-290	Polycrystal (grain 5 to 12 mm)	$1.0 \cdot 10^{-2}$
Nb-660	Polycrystal (grain 5 to 12 mm)	$4.5 \cdot 10^{-3}$
Nb-970	Polycrystal (grain 5 to 12 mm)	$3.0 \cdot 10^{-3}$
Nb-2100	Single crystal $\langle 100 \rangle$	$1.4 \cdot 10^{-3}$ Nb-10000
Fe	Single crystal $\langle 731 \rangle$	$< 1.0 \cdot 10^{-4}$

corded in temperature interval of 28 to 35 K [22–24]. It was supposed [18] that the peaks in Fe observed in [14–16, 22–24] are of the same physical origin, that is, the resonance interaction of elastic vibrations with thermally activated nucleation of kink pairs at non-screw dislocations.

The effect of plastic deforming, thermo-cycling, and low-temperature annealing on parameters of low-temperature internal friction α -peak and the related Young's modulus defect in niobium single crystals and polycrystals with different total impurity concentrations, c , as well as in high-purity iron single crystals was studied using mechanical spectroscopy at frequencies of about 90 kHz.

The Nb samples were shaped as rectangular parallelepipeds of $3 \times 3 \times 21$ mm³ size. Those were cut out of niobium single crystals and polycrystals of different purity grades using spark erosion, then ground to the required shape and size using abrasive powders and chemically polished to remove surface layers damaged by machining. The crystallographic orientation of the single crystal sample longitudinal axis was determined to within $\pm 1^\circ$ using Laue diffraction patterns.

The polycrystals had coarse-grain bamboo-type structure, that is, the sample cross-section dimensions (3×3 mm²) were smaller than the grain size (5 to 12 mm). The initial dislocation density in the samples was of 10^5 to 10^6 cm⁻². The spectral analysis has shown that the main substitution impurities were Mo, Ta, and Zr atoms. The amount of N, O, and H interstitial impurities was minimized by prolonged high-temperature annealing first in oxygen flow at a pressure of about 10^{-3} Pa, and then in ultrahigh vacuum (about 10^{-8} Pa) [25]. The reduced residual electric resistance

$RRR = R_{300}/R_0$ was used as an integral measure of the sample purity; the RRR values for metallic solid solutions are well-known to be in inverse proportion to the impurity concentration. To determine RRR , temperature dependences of the sample resistance were measured in 2 to 300 K temperature range, and then the experimental data obtained were extrapolated to 0 K and zero external magnetic field that was used to convert the samples into normal state at temperatures lower than the superconductive transition point, $T_c \approx 9.3$ K [26].

The Fe sample shaped as a 27 mm long cylindrical rod of 4 mm diameter was cut out of a high-purity single crystal grown by recrystallization method [27]. The high purity of the sample was attained by 7-fold zone melting of the initial commercial metal (Johnson & Mattheu, Great Britain) and prolonged (about 7 days) annealing of the grown single crystal in anhydrous hydrogen with heated zirconium absorbent [28]. The final content of interstitial impurities (C, N, etc.) was less than $1 \cdot 10^{-4}$ % (at.). The initial density of growth dislocations was of 10^5 to 10^6 cm⁻². To establish the relationship between the acoustic properties and dislocation processes, fresh dislocations were introduced into the sample at room temperature by plastic deforming using four-point bending, the sample remaining glued to the piezoelectric transducer. The plastic strain measure was the residual outside-line deformation, $\varepsilon_{pl} \approx 3$ %.

The Fe sample orientation was determined using Laue diffraction pattern; the longitudinal sample axis was coincident with the longitudinal sound wave vector and with the loading axis at plastic deforming. Its direction was close to $\langle 731 \rangle$ coplanar with $\langle 111 \rangle$ and $\langle 101 \rangle$ ones and making about 45° angles therewith. The chosen sample orientation provided singlet sliding

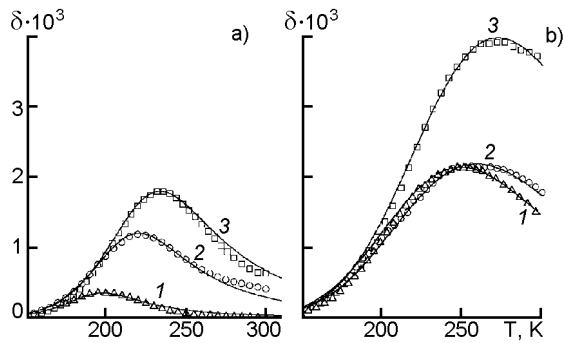


Fig. 1. α -peak in coarse-grain niobium polycrystals with various impurity content (a—the 1st cooling 300–150 K; b—1st re-heating 150–300 K): Nb-970 (1), Nb-660 (2), Nb-290

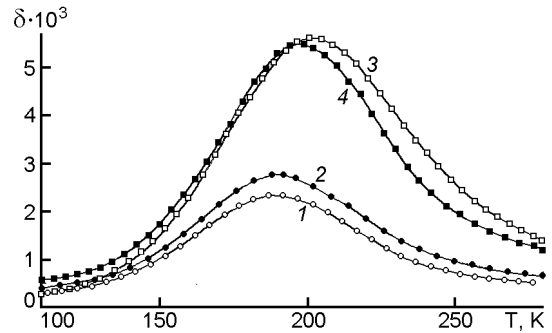


Fig. 2. Effect of the Nb-60 sample structure on the α -peak: 1st thermocycling (300–6–300 K) of non-deformed sample (1); 1st thermocycling (300–6–300 K) (2); plastic deforming, $\epsilon_{pl} = 5\%$ (3); 1 year exposure of deformed sample at 300 K (4).

in the (101) plane with maximum resolved stress in the Burgers vector direction [111] [29]. The main characteristics of the samples are presented in Table 1.

Acoustic measurements were made by two-composite vibrator method [30, 31]. Longitudinal standing waves of 90 kHz frequency were excited in the sample. The ultrasonic strain amplitude in our experiments was $\epsilon_0 \sim 10^{-7}$, thus answering to amplitude-independent acoustic relaxation. Under the sample cooling and heating at a rate of about 1 K/min within temperature range $6\text{ K} < T < 310\text{ K}$, temperature dependences of the sample logarithmic decrement δ and resonance frequency of the composite vibrator. Using the latter parameter, the dynamic elastic Young modulus E was calculated [31].

The relaxation resonance localization temperature (T_p) and its characteristic width (T_h) in Nb and Fe have been found to depend on the sample structure state that was varied by plastic pre-deforming at room temperature (Nb and Fe, Fig. 1 and 2) and thermocycling (Nb, Fig. 2) as well as by varying the impurity concentration (Nb, Fig. 3). Increasing Nb sample purity results in elevated peak localization temperature as well as in increased width and amplitude thereof.

Evolution of temperature dependences of the vibration decrement and dynamic elastic modulus resulting from plastic deforming followed by low-temperature annealing is due to introduction of fresh dislocations into the sample. The fresh dislocations, at the one hand, act as relaxators: kink pairs arise thereon in a fluctuation manner. The acoustic vibration resonance with this process causes the relaxation peak. At the other hand, chaotic distribution of dislocations

results in statistical distribution of internal stress local fields and of the kink pair parameters in the sample volume. In the course of annealing, a partial relaxation of the dislocation structure and long-range internal stress fields associated with dislocations takes place. It can be shown [13, 21, 32] that various actions on the sample causing structure changes may change the parameters of the statistical distribution of activation energy U of the process responsible for the acoustic absorption peak. In this case, increased dispersion of the activation energy results in the peak broadening and the peak localization temperature shift towards higher values. It is obvious that the reduced dispersion (resulting from the sample annealing) causes an opposite result. The temperature dependence of the modulus defect is subjected to corresponding changes.

It has been shown [13, 21, 32] that, at statistical distribution of activation energy values, instead of Debye temperature spectrum of relaxation (typical of an ideal crystal)

$$\frac{\Delta M(\omega)}{M_\infty} = \frac{M_\infty - M_1(\omega)}{M_\infty} = \frac{\Delta_r}{1 + \omega^2\tau^2}, \quad (1)$$

$$Q^{-1}(\omega) = \frac{M_2(\omega)}{M_\infty} = \Delta_r \frac{\omega\tau}{1 + \omega^2\tau^2},$$

where $\Delta M(\omega)/M_\infty$ is the susceptibility (modulus) defect; M_∞ , the unrelaxed susceptibility; $Q^{-1}(\omega)$, inverse mechanical quality; $\Delta_r = C_r\Delta_0$, the relaxation force; Δ_0 , characteristic dimensionless elementary contribution to the material dynamic response; C_r , relative dimensionless volume concentration of elementary relaxators interacting with

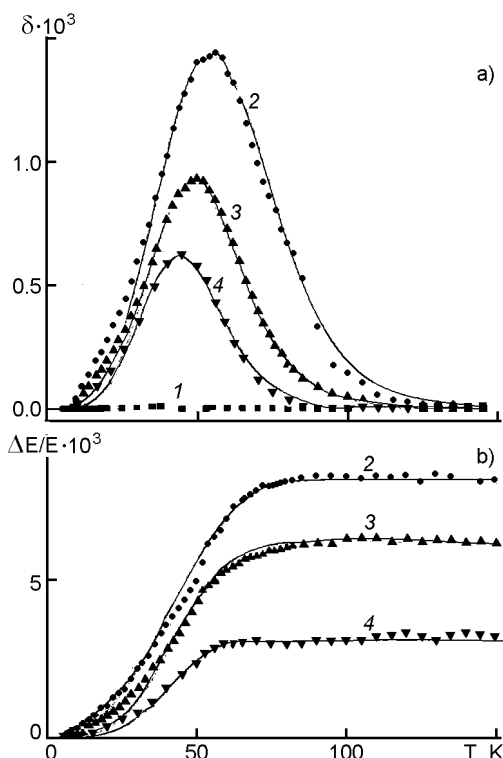


Fig. 3. Temperature dependences of decrement δ (a) and modulus defect $\Delta E/E$ (b) in Fe: non-deformed sample (1); plastic deforming, $\epsilon_{pl} \approx 3\%$ (2); 3 days exposure of deformed sample at 300 K (3); 11 years exposure of deformed sample at 300 K (4).

the sample vibration mode under consideration; in the case of thermally activated relaxation process with the relaxation time

$$\tau(T) = \tau_0 \exp(U_0/kT), \quad (2)$$

where τ_0 and U_0 are the attempt period and activation energy of elementary relaxer, respectively; k , the Boltzmann constant; T , temperature; the dynamic response of a crystal containing defects is characterized by average on a spectrum of activation energy

$$P(U, U_0, D) = \frac{1}{\sqrt{2\pi}DU_0} \exp\left(-\left[\frac{U - U_0}{\sqrt{2}D}\right]^2\right) \quad (3)$$

$$\int_0^\infty P(U, U_0, D) dU = 1$$

by response functions

$$\frac{\Delta M}{M_\infty} = \Delta_r \mu^{(1)}(T, \omega, \tau_0, U_0, D) \text{ and}$$

$$\bar{Q}^{-1} = \Delta_r \mu^{(2)}(T, \omega, \tau_0, U_0, D);$$

where

$$\mu^{(1)} = \int_0^\infty \frac{1}{1 + \omega^2 \tau_0^2 \exp\left(\frac{2U}{kT}\right)} P(U, U_0, D) dU \text{ and} \quad (4)$$

$$\mu^{(2)} = \int_0^\infty \frac{\omega \tau_0 \exp\left(\frac{U}{kT}\right)}{1 + \omega^2 \tau_0^2 \exp\left(\frac{2U}{kT}\right)} P(U, U_0, D) dU.$$

The functions $\mu^{(1)}$ and $\mu^{(2)}$ are convenient to be presented as

$$\mu^{(1)} = \Omega \cdot \chi \cdot \int_1^\infty \frac{dx}{x} f(x, \theta, \Omega, d) \quad (5)$$

$$\mu^{(2)} = \chi \cdot \int_1^\infty dx \cdot f(x, \theta, \Omega, d)$$

$$f(x, \theta, \Omega, d) = \frac{1}{2} \cdot \frac{\ln x}{\Omega^2 + x^2} \cdot \exp\left(-\left[\frac{\theta \ln x - \ln \Omega}{d}\right]^2\right)$$

$$\chi = \frac{2\Omega\theta^2}{\sqrt{\pi} d \ln \Omega}.$$

Here, $\theta = T/T_p^{(0)}$ is the dimensionless temperature; $\Omega = 1/\omega\tau_0$, inverse dimensionless frequency; $d = \sqrt{2}D/kT_p^{(0)}$, dimensionless dispersion characteristic.

Consideration of expressions (5) shows that the resonance localization temperature T_p and the absorption peak width T_h measured at half-height of its maximum amplitude are related to the elementary relaxation parameters by the following relationships:

$$T_p = T_p^{(0)} \cdot \left[1 + \frac{D^2}{U_0^2}\right], \quad (6)$$

$$T_h = T_h^{(0)} \cdot \left(1 - \frac{D}{\sqrt{2}U_0} \ln \omega \tau_0\right).$$

It follows from the expression for T_p that τ_0 can be estimated basing on the activation plot:

$$\ln \omega = \ln \tau_0^{-1} - \frac{U_0^2 + D^2}{U_0} \cdot \frac{1}{kT_p}.$$

Formulas making it possible to determine U_0 and D using the known $\omega\tau_0$ value and experimental data on T_p and T_h have the form

Table 2. Empirical estimations of activation parameters (U_0 , D , and τ_0) of relaxation process responsible for the α -peak in Nb

Sample	T_p , K	T_h , K	$10^{10} \cdot \tau_0$, c	U_0 , eV	$10^2 \cdot D$, eV
Nb-60	189 ⁽¹⁾ , 190 ⁽²⁾	65.2 ⁽¹⁾ , 65.5 ⁽²⁾	1.0	0.15	0.78 ⁽¹⁾ , 0.79 ⁽²⁾
	202 ⁽³⁾ , 197 ⁽⁴⁾	74.4 ⁽³⁾ , 65.7 ⁽⁴⁾			0.98 ⁽³⁾ , 0.67 ⁽⁴⁾
Nb-290	198 ⁽⁵⁾ , 251 ⁽⁶⁾	55 ⁽⁵⁾	3.0		0 ⁽⁵⁾ , 2.65 ⁽⁶⁾
Nb-660	221 ⁽⁵⁾ , 255 ⁽⁶⁾	78 ⁽⁵⁾	6.7		0 ⁽⁵⁾ , 2.68 ⁽⁶⁾
Nb-970	234 ⁽⁵⁾ , 275 ⁽⁶⁾	79 ⁽⁵⁾	11.0		0 ⁽⁵⁾ , 2.42 ⁽⁶⁾
Nb-37 ⁽⁶⁾	226	86	0.8		2.42
Nb-2100 ⁽⁷⁾	255	81	2.8		3.0
Nb-10000 ⁽⁶⁾	265	–	16.0		1.76

(¹) single thermocycle, (²) repeated thermocycling, (³) plastic deforming, $\epsilon_{pl} = 5\%$, (⁴) anneal at 300 K for 365 days, (⁵) 1st cooling, (⁶) 1st re-heating, (⁷) plastic deforming, $\epsilon_{pl} = 15\%$, after prolonged anneal, 1st cooling.

$$U_0 = \frac{k(\ln\omega\tau_0)^3}{2(2 + (\ln\omega\tau_0)^2)} \times \quad (7)$$

$$\times \left(-T_p + \frac{2T_h}{\ln\omega\tau_0} - \sqrt{T_p^2 - \frac{4T_p T_h}{\ln\omega\tau_0} - 2T_h^2} \right)$$

$$D = \frac{\sqrt{2}k(\ln\omega\tau_0)^2}{4(2 + (\ln\omega\tau_0)^2)} \times \quad (8)$$

$$\times \left(-T_p - T_h \ln\omega\tau_0 - \sqrt{T_p^2 - \frac{4T_p T_h}{\ln\omega\tau_0} - 2T_h^2} \right)$$

The relaxation force Δ_r can be found from the condition

$$\frac{\Delta \bar{M}(T)}{M_\infty} \Bigg|_{T \gg T_p}^{(experiment)} = \quad (9)$$

$$= \mu^{(1)}(T, \omega, \tau_0, U_0, D) \Big|_{T \gg T_p} \cdot \Delta_r = \Delta_r.$$

It has been found that the ratio of temperature derivatives in the function inflexion points $\mu^{(2)}(\theta, \Omega, d)$ has the same value $K = -\max \left[\frac{\partial \mu^{(2)}}{\partial \theta} \right] / \min \left[\frac{\partial \mu^{(2)}}{\partial \theta} \right]$ that depends significantly on the Ω parameter but is essentially independent of the dispersion parameter d and permits the analytical approximation $K(\Omega) = 1 + 10/(\ln\Omega)^2$. This formula makes it possible to find the parameter τ_0 basing on the peak shape only and doing no experiments with varying frequency ω .

The processing of experimental data allowed to estimate empirically the activation parameters (U_0 and τ_0) that characterize the relaxation process responsible for the α -peak

Table 3. Activation parameters of relaxation process responsible for the α -peak in Fe

Peak (plateau) parameters	Sample structure state		
	2	3	4
T_p , K	54.3	49.5	44.4
T_h , K	41.8	36.1	28.5
D , eV	0.018	0.015	0.014
U_0 , eV	0.037		
τ_0 , c	$2.5 \cdot 10^{-11}$		

The sample structure states are numbered as in Fig. 3.

in Nb and Fe as well as the activation energy dispersion values D corresponding to various structure states of the samples (Tables 2 and 3). The effect of impurity content on α -peak parameters in Nb is due to τ_0 dependence on the impurity concentration (see Table 2).

Consideration of the whole experimental data set obtained at the study of the α -peak in niobium allows us to conclude that the peak results from resonance interaction of the sample elastic vibrations with the process of thermally activated generation of kink pairs at dislocation segments lying in the valleys of the Peierls potential relief.

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Структурна чутливість параметрів α -піку акустичної релаксації у ніобії та залізі

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На моно- та полікристалах ніобію з різним вмістом домішок, а також на монокристалах чистого заліза експериментально вивчено вплив зміни дислокаційної структури зразків на параметри низькотемпературного α -піку внутрішнього тертя та відповідного йому дефекту модуля Юнга. Запропоновано статистичну інтерпретацію температурної залежності та структурної чутливості характеристик динамічної релаксації в області α -піку, яка базується на припущенні про наявність випадкового розкиду значень енергії активації елементарних релаксаторів. Отримано емпіричні оцінки для періоду спроб, середнього значення та дисперсії енергії активації релаксаційного процесу, що відповідає за α -пік у вивчених матеріалах.