Peculiarities of the dynamics of a nonlinear oscillator in a constant-temperature chamber and the possible inadequacy of the phonon picture in β-zirconium

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(Submitted 26 October 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 10, 542–546 (25 November 1992)

The stochastic equations of motion of a particle in a bistable potential have been studied numerically for the case in which the temperature is comparable with the height of the potential barrier. Analysis of the results of this study makes it possible to give a qualitative explanation of a number of unusual features of the lattice dynamics of Ti and Zr and their alloys.

Recent experiments on inelastic neutron scattering in Ti and Zr have once again attracted interest in the long unsolved problem of describing the lattice dynamics under conditions of strong anharmonicity near a structural instability. As far back as 1975–76 (Refs. 2 and 3) a number of unusual phenomena were detected in $Zr_{1-x}Nb_x$ alloys: a central peak in the neutron scattering and a "symmetry-forbidden splitting of the phonon branches,"[2] and also anomalies in the quasielastic scattering of Mössbauer radiation.[3] In Ref. 1 it was shown that the transverse phonon branches in the high-temperature β phase (*bcc*) of pure Ti and Zr in the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions, associated respectively with the $\beta-\alpha$ (*hcp*) and $\beta-\omega$ transitions are poorly defined, and instead of a "central peak," characteristic of alloys, a distribution of the scattered neutrons over the transferred energy is observed. The present paper is dedicated to a discussion of these phenomena.

In general, anharmonic effects in any crystal can be considered in the framework of perturbation theory in the adiabatic parameter as effects of weak nonideality of the phonon gas. However, for selected vibrational modes in metals, near the structural instability, the anharmonicity of the potential energy V can be very strong (see the review article in Ref. 4). This is confirmed by direct calculation by the frozen- phonon method for various deformations of the lattice in β-Zr[5,6] and Ba.[7] Figure 1 shows a graph of $V(x)$ for deformations x corresponding to a longitudinal phonon with wave vector $\mathbf{q}=\frac{2\pi}{a}(\frac{2}{3},\frac{2}{3},\frac{2}{3})$, which is associated with the β–ω transition, (a is the lattice constant) and the transverse phonon with $\mathbf{q}=\frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},0)$, which is associated with the β–α transition. In the first case the deep minimum corresponds to the ω-phase, and the shallow one, to the β-phase, which indicates that β-Zr is unstable at $T=0$ with respect to the β–ω transition [the potential $V(x)$ is symmetric about the minimum]. In the second case the maximum of $V(x)$ at $x=0$ indicates that β-Zr is unstable at $T=0$ with respect to the β–α transition. The problem of lattice dynamics with these potentials is a model-based problem, since the β-phase, which is stabilized as a result of entropy contributions at high T, was actually investigated in Refs. 1 and 2. Unfortunately, a

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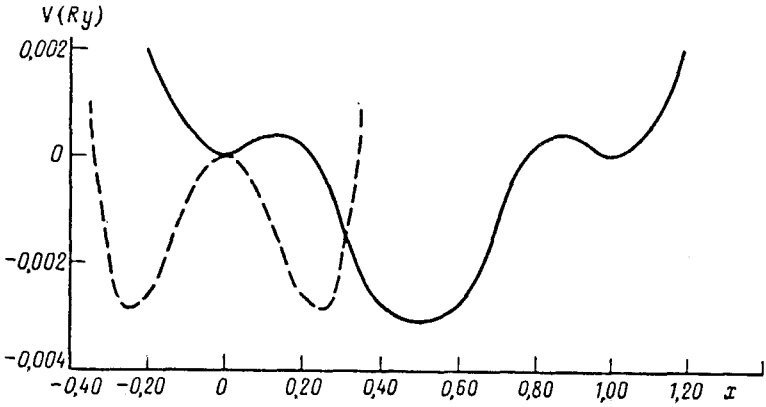


FIG. 1. Dependence $V(x)$ in β-Zr for a longitudinal phonon with $\mathbf{q}=\frac{2\pi}{a}(\frac{2}{3},\frac{2}{3},\frac{2}{3})$ (solid curve)[5] and for a transverse phonon with $\mathbf{q}=\frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},0)$ (dashed curve);[6] x is in units of the interplanar distance d ($d = a\sqrt{3}/6$ and $d = a/\sqrt{2}$, respectively).

rigorous calculation of the type carried out in Refs. 5–7 with these contributions taken into account has been so far impossible. However, it can be assumed that such features of $V(x)$ as its bistability and the order of magnitude of the barrier height are characteristic of metals and alloys near the martensitic transitions.

Our simple model of the lattice dynamics with potential $V(x)$ takes into account the interaction of a selected vibrational mode (corresponding to the collective variable x) with the remaining phonon degrees of freedom by introducing the phenomenological extinction parameter γ and the random force $F(t)$ in the spirit of the Langevin equation for Brownian motion.[8] We express x in units of the interplanar distance d and introduce the dimensionless quantities $\bar{\gamma}=\gamma/m\omega_0$, $f=F/md\omega_0$, $\bar{V}(x)=V(x)/\alpha d^2$, and $\tau=t\omega_0$, where m is the atomic mass of Zr, $\alpha = d^{-2}\partial^2 V/\partial x^2|_{x=x_0}$ and x_0 is the position of the minimum in the β phase (at the β–ω transition) or in the α phase, and $\omega_0 = \sqrt{\alpha/m}$ is the frequency of the corresponding phonon. The dynamics of the selected variable is described by the stochastic equation

$$\frac{d^2x}{d\tau^2}=-\frac{d}{dx}\bar{V}(x)-\bar{\gamma}\frac{dx}{d\tau}+f(\tau), \tag{1}$$

where $f(\tau)$ is Gaussian white noise:

$$\langle f(\tau)f(\tau')\rangle=2\bar{\gamma}T\delta(\tau-\tau'). \tag{2}$$

Here the temperature T is expressed in the units αd^2. Given condition (2), Eq. (1) describes relaxation of the distribution function $P(x,\tau)=\langle\delta[x-x(\tau)]\rangle$ to the equilibrium value[8] $P_0(x)\sim\exp[-V(x)/T]$.

By virtue of the anharmonicity of the potential $V(x)$, the frequency spectrum

$$S(\omega)=\int_{-\infty}^{\infty} d\tau\langle x(\tau)x(0)\rangle\exp(i\omega\tau), \tag{3}$$

describes a wide distribution even for $\tilde{\gamma}=0$. Indeed, if $\Omega(H)$ is the frequency of the oscillations with energy H, where $\Omega(H)=2\pi/T_0(H)$, where $T_0(H)$ is the period of the oscillations, then we have

$$S_0(\omega)\propto \int \frac{dH}{\Omega(H)}\exp\left(\frac{H}{T}\right)\delta[\omega-\Omega(H)]. \tag{4}$$

Since $H=H_c$ and $\Omega(H)\propto[\ln(H_c/|H-H_c|)]^{-1}$ near the separatrix, we have in the limit $\omega\to 0$

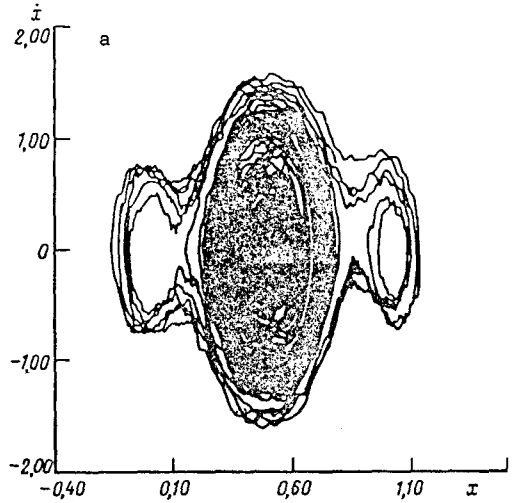
$$S_0\omega\propto\frac{1}{w^3}\exp(-\text{const}/w). \tag{5}$$

By virtue of relation (4), the spectrum $S(\omega)$ extends from $\omega=0$ to $\omega=\Omega_{\max}$. Therefore, in order to obtain, in agreement with the experimental data,[1] a wide frequency distribution with prescribed $q=Q$, it is not necessary to assume the extinction γ to be unusually large; we will choose $\tilde{\gamma}$ in the interval 10^{-2}–10^{-1}, which is characteristic of phonons in metals at high temperatures.[9]

The standard method of investigating Eq. (1) is to solve the corresponding Fokker–Planck equation for $P(x,\tau)$ for the case in which the transition time between the wells t_{tr} is large in comparison with ω_0^{-1} (see Ref. 8). In the interesting case in which T is of the order of the barrier height ($\Delta E=0.004$ mRy for the β–ω transition in Zr[5]) the problem must be solved numerically.

The dynamics of the investigated system were modeled by solving Eq. (1) numerically, using the method of direct integration of the stochastic equations.[10] In the Fourier transform (3) $x(\tau)$ is replaced by $x(\tau)-\bar{x}$, where $\bar{x}$ is the mean displacement during the integration time. In this way the contribution to $S(\omega)$ of static displacements of the form $\bar{x}\delta(\omega)$ is eliminated from consideration.

Figure 2a shows the typical form of the phase portrait $\dot{x}(x)$ for the β–ω transition at $T=0.6\Delta E$. It is possible to distinguish three types of phase trajectories and associated characteristic frequencies: 1) trajectories corresponding to motion in the upper (β) well with frequency $\omega_\beta\approx\omega_0$; 2) trajectories in the lower (ω) well with frequency $\omega_\omega\approx 0.8\omega_0$; 3) "migratory" trajectories, encompassing both wells with frequency $\omega_{\beta\omega}\approx 0.35\omega_0$. This picture corresponds to a time interval on which the system spends a large part of its time in the central (ω) and left (β) wells. Figure 2b shows the spectral density $S(\omega)$, obtained during the modeling interval $\tau=1000$. In addition to the pronounced peaks near $\omega=\omega_\omega$ and $\omega=\omega_{\beta\omega}$, we see a frequency band which extends all the way to $\omega=0$. Such a band is formed when the trajectories pass in the immediate vicinity of the separatrix. The significant contribution to $S(\omega)$ of these trajectories is due to the long time the system spends ($\dot{x}\approx 0$) above the potential barrier during the transition from one state to the other. Note that the dynamics of the system in the β-state contributes almost nothing to the spectral density [$S(\omega_\beta)\approx 0$], because of the extraordinarily short residence time in the upper well.



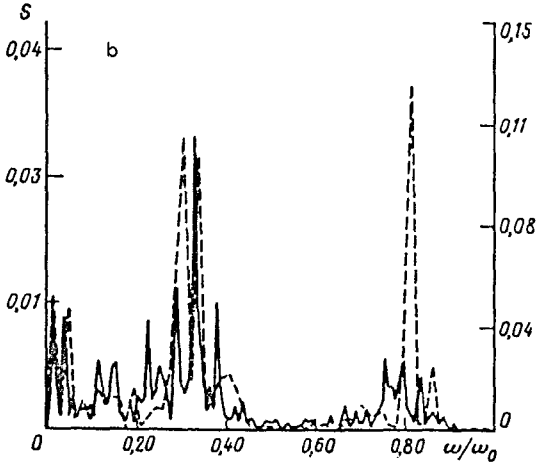
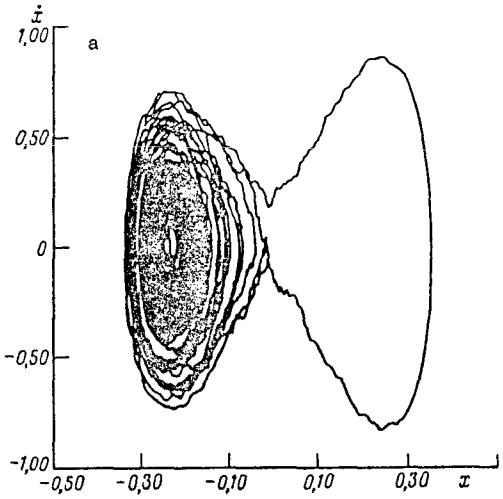


FIG. 2. Phase portrait (a) and spectrum $S(\omega)$ (b) for the mode corresponding to the β–ω transition for $T=0.6\Delta E$, $\tilde{\gamma}=0.075$. The dashed curve in b shows the spectrum at $T=0.5\Delta E$ and the same value of $\tilde{\gamma}$ (corresponding vertical axis—to the right).

As the above calculations show, at decreased temperatures ($T\leqslant 0.5\Delta E$) the system spends almost all its time in the ω well. With increase of the temperature, the contribution of the trajectories lying above the separatrix ($\omega\sim\omega_{\beta\omega}$) increases and for $T\geqslant 0.7\Delta E$ predominates. Decrease of the magnitude of the extinction (from 0.065 to 0.085), while not changing the overall picture, enhances the contribution of the low-frequency dynamics.

Figure 3 shows analogous results for the mode associated with the β–α transition.



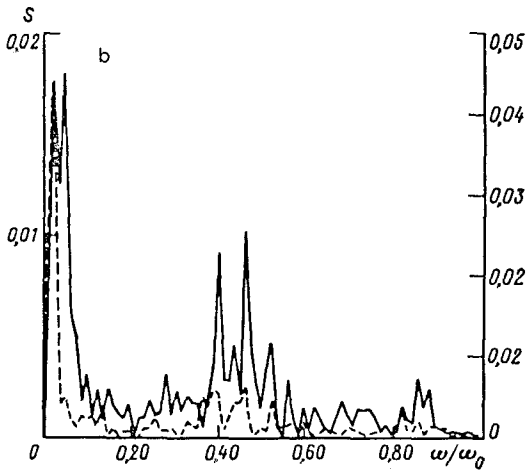


FIG. 3. Phase portrait (a) and spectrum $S(\omega)$ (b) for the mode corresponding to the β–α transition for $T=0.55\Delta E$, $\bar{\gamma}=0.065$. The dashed curve in b shows the spectrum at $T=0.45\Delta E$ and the same value of $\bar{\gamma}$ (corresponding vertical axis—to the right).

In this case the "phonon" contributions to $S(\omega)$ (which are associated with oscillations in one of the wells) are even less important and nearly the entire spectral density is due to the open trajectories.

Upon lowering the temperature to $T\leqslant(0.2\text{–}0.3)\Delta E$, the standard picture of the spectrum, which consists of a phonon peak at $\omega=\omega_0$ (or two peaks for an asymmetric potential well) and a central peak associated with the rare transitions between the wells, is reconstructed.

Two qualitative results which are most important for interpretation of experimental data may be singled out.[1,2] In general, it can be assumed that even strong anharmonicities reduce to a renormalization and possibly to a splitting of phonon frequencies. In fact, at $T \geqslant 0.5\Delta E$, the main contribution to the spectral density comes from the open trajectories, which are basically outside the scope of the description of the lattice dynamics in terms of phonons. In an interpretation of experimental results the corresponding peaks in $S(\omega)$ $\omega \simeq (0.3\text{–}0.4)\omega_0$ in the models we have considered may be erroneously attributed to the appearance of additional "soft" phonon branches. This may be the real reason for the symmetry-forbidden phonon splitting in Zr–Nb alloys,[2] which is accompanied by a significant broadening of the phonon branches.

Another important result is the transition from a nonphonon-type spectrum to a usual one (one with frequency splitting and a central peak) with decrease of the temperature. According to Ref. 1, the latter is characteristic of titanium and zirconium alloys in contrast to the pure metals. The simplest explanation of this fact would be that in pure Ti and Zr the β-phase is stable at higher temperatures, and the difference in the dynamics of the metals and the alloys is due simply to the parameter $T/\Delta E$, to which the form of $S(\omega)$ is very sensitive.

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Translated by P. F. Schippnick