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Phonons and martensitic phase transitions in pure bcc Ti and bcc Zr

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Phonons have been measured in β-Ti and β-Zr over the whole range of existence of the high-temperature bcc phase. Low-frequency and strongly damped longitudinal phonons at $\mathbf{q}=\frac{2}{3}(111)$ produce the necessary displacements for the martensitic β-ω transition. The displacements needed for the martensitic β-α transition are produced by low-frequency and damped transverse phonons at $\mathbf{q}=\frac{1}{2}(110)$, which on approaching the phase transition soften further but not completely. The low-frequency and strongly damped phonons are precursor fluctuations of the α or ω phase within the β phase.

Recently, a number of first-principles studies have been published on the dynamics of martensitic phase transitions (MT) in pure metals. Ye *et al.*[1] studied the stability of the high-temperature bcc phase of Zr by frozen phonon calculations taking into account anharmonicities to the fourth order. Using the same technique the pressure-induced (bcc to hcp) transition in Ba was investigated by Chen, Ho, and Harmon.[2] Lindgard and Mouritsen[3] considered a Landau expansion of the free energy of Zr in terms of two fluctuating strains and Dmitriev *et al.*[4] extended this expansion in a general way including the bcc to ω transition. Krumhansl and Gooding[5] showed that small changes of an already low but nonzero frequency mode are sufficient to drive the MT. Molecular dynamic simulations of a highly anisotropic system[6] indicated the importance of low-frequency phonons distributed over a wide range of energy in driving the actual phase transformation. All these investigations predict precursor effects in terms of particular low-frequency phonons which further decrease when the phase transition is approached from high temperature. Furthermore, they predict areas of metastable domains of the new phase which have a relatively long lifetime. In a neutron experiment the precursor effects should manifest themselves in (over) damped low-frequency phonons while the second part should appear in a way similar to the central peak phenomenon as scattering around $\hbar\omega=0$. Within the experimental energy resolution this appears as "elastic" intensity.

Neutron scattering experiments on *metal alloys* have revealed such pronounced temperature-dependent phonon softening and diffuse scattering around the transition temperature T_0.[7] In these systems defects may play an important role. Neutron studies of these precursor effects in *pure metals* are known for Na,[8] K,[9] Li,[10] Co,[11] and Tl.[12] In contrast to the alloys, there is no, or only a weak softening of, particular phonons; in Li and Na small q phonons become even harder when T_0 is approached. No elastic precursors or charge-density-wave satellites have been found in Na and K. Li and Co show strong satellites above T_0 which have been explained by the coexistence of the low-temperature phase.

Here we report on the first study of the temperature dependence of elastic and inelastic scattering in the bcc phase of the group-four metals, Ti and Zr, with special attention to their MT's. By lowering the temperature the bcc lattice transforms to hcp ($T_0=882°$ and 865 °C for Ti and Zr, respectively) and under pressure the trigonal ω structure [typical pressures at room temperature of 40 kbar (Ref. 13)] can be obtained. These systems are particularly well suited to study the dynamics of phase transitions because (i) the parent bcc phase is of extreme simplicity and transforms martensitically into either of two new phases, (ii) T_0 occurs at high temperature; consequently thermal equilibrium is always achieved during the

measurements, and (iii) theory[1-6] explicitly refers to these materials as model cases for bcc-hcp and bcc-ω transitions. However, these elements are extremely difficult to obtain as bcc single crystals as they have to be grown and orientated *in situ* on the spectrometer.[14]

As shown by Burgers,[15] the following relations hold for the bcc (β) to hcp (α) transition:

$$(110)_\beta \| (00.1)_\alpha, \quad \text{and} \quad [\bar{1}11]_\beta \| [\bar{2}1.0]_\alpha .$$

For a given bcc orientation, twelve possible variants of the resulting hcp structure can occur. This transformation can be achieved by an alternating displacement of neighboring (110) planes in opposite $[1\bar{1}0]$ directions to obtain the hcp stacking sequence and by two equivalent long-wavelength shears—for instance $(1\bar{1}2)[\bar{1}11]$ and $(\bar{1}12)[1\bar{1}1]$—which squeeze the lattice into the final hexagonal basal plane. The β to ω transformation is performed by a collapse of two neighboring {111} planes, while every third plane stays at rest, and is described by the crystallographic relation:[16]

$$(111)_\beta \| (00.1)_\omega, \quad \text{and} \quad [\bar{1}01]_\beta \| [01.0]_\omega .$$

There exist four possible variants of the trigonal ω structure. It is thus expected that precursors of the β-α transition can be found in the $T_1A[\xi\xi 0]$ phonon branch with $[1\bar{1}0]$ polarization for $\xi \rightarrow 0.5$ and those of the β-ω transition in the $LA[\xi\xi\xi]$ branch at $\xi = \frac{2}{3}$.

Single crystals of β-Ti and β-Zr of roughly 1 cm in diameter and 4 cm in length were grown *in situ* by zone-melting technique and orientated without intermediate cooling. Analysis of the starting material, rods of 4*N* Ti, supplied by MRC France and 3*N*5 Zr, supplied by Teledyne Wah-Chang, by Bundesanstalt für Materialprüfung, Berlin, showed contamination of oxygen and nitrogen of 547(23)/97(7) wt ppm in Ti and 31(5)/4(1) wt ppm in Zr. The experiments were performed on several crystals of β-Ti and β-Zr, on the triple-axis spectrometer IN8 at the high flux reactor of the Institut Laue-Langevin, Grenoble. The complete phonon dispersion of β-Ti has been measured at 1020 °C, and has been reported elsewhere.[17] The phonon dispersion curve of β-Zr was measured at 950 °C and agrees well with those measured first by Stassis, Zarestky, and Wakabayashi.[18] As a result, the dispersion of both elements overlap within experimental error when scaled to the square root of the atomic mass and to the lattice parameter (Lindemann homology rule). As precursors of the β-α transition and the β-ω transition, respectively, the $T_1A[\xi\xi 0]$ branch is indeed low and the $LA[\xi\xi\xi]$ branch has a pronounced dip at $\mathbf{q} = \frac{2}{3}(111)$. Below we present the first study on the temperature dependence of these two branches over the whole range of existence of the bcc structure in both elements.

β-ω transition: Constant energy scans in β-Zr [Fig. 1(a)] and β-Ti (Fig. 3, Ref. 17) around the ω-point show that phonon intensity can be observed down to zero-energy transfer. The elastic intensity at $\hbar\omega = 0$ meV, however, does not differ from the inelastic intensity at, for example, 6 meV implying that no superstructure peak is found at $\mathbf{q} = \frac{2}{3}(111)$, i.e., only fluctuations into the ω-phase are observed and within the time window of the instrument ($\leq 10^{-11}$ sec) no stable ω embryos exist.

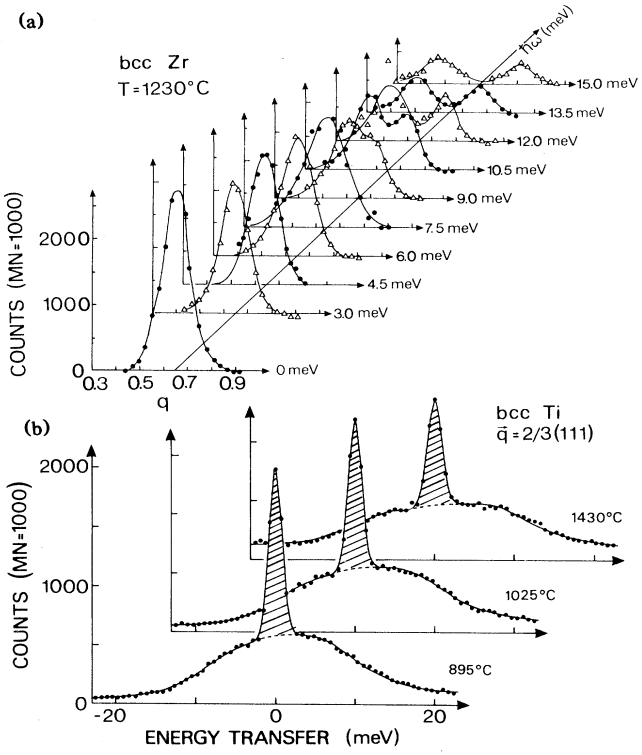

FIG. 1. (a) Constant $\hbar\omega$ scans in β-Zr along $\mathbf{Q} \| [\xi\xi\xi]$ for different neutron energy losses $\hbar\omega$. For $\hbar\omega = 0$, the measured *incoherent* scattering has been subtracted. All fits give a Gaussian linewidth (FWHM) of 0.10 rlu. (b) Uncorrected constant q scans in β-Ti at $\mathbf{Q} = 1.35(111)$ at various temperatures. All spectra fit to the same damped oscillator of FWHM = 15(8) meV and a center of 11(1) meV. The asymmetry of the spectra is purely instrumental. The shaded area indicates the elastic incoherent scattering.

As indicated by the (full width at half maximum) FWHM = 0.1 rlu (reciprocal lattice units) of the phonon groups this weakness of the bcc structure is well defined in $\mathbf{q}$ space. In energy the inelastic intensity extends over a large range, best demonstrated by a constant q scan at $\mathbf{q} = \frac{2}{3}(111)$. Besides the purely incoherent elastic peak, Fig. 1(b) shows broad inelastic shoulders which can be fitted by a damped oscillator.[19] At the ω point, phonons are strongly damped and have a lifetime of 0.8×10^{-13} sec for β-Ti and 1.4×10^{-13} sec for β-Zr or in a physically equivalent picture show a large distribution of vibrational energies extending from almost zero to 15 meV in β-Ti and 10 meV in β-Zr. Within the accuracy of the experiments we could not detect any temperature dependence of the shape of these broad shoulders [Fig. 1(b)]. With respect to the degree of softening the temperature is a less relevant parameter, in agreement with the pressure-temperature phase diagram of group-four elements;[13] the ω phase is stable only under high pressure and, therefore, a further softening of the phonons at $\mathbf{q} = \frac{2}{3}(111)$ is expected under pressure.

The weakness towards ω fluctuations is an intrinsic bcc property. For this mode the atomic motion can be viewed

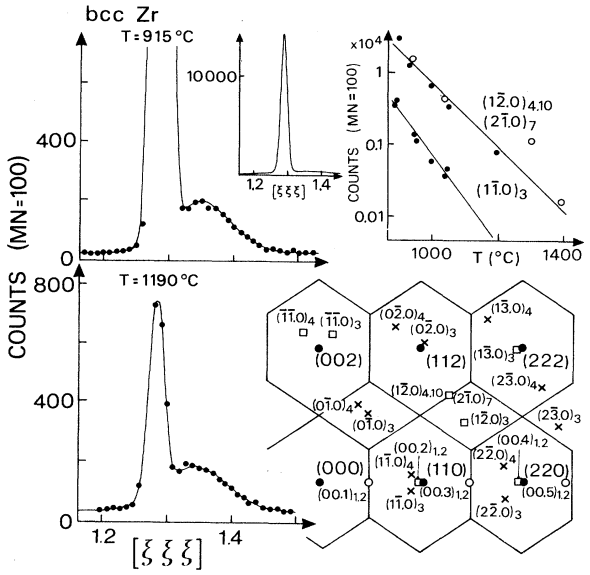

FIG. 2. Left-hand side: Elastic measurements in β-Zr along $\mathbf{Q}\parallel[\xi\xi\xi]$. The intensity of the α peak at $\mathbf{Q}=1.28(111)$ depends on temperature, whereas the ω intensity at $\mathbf{Q}=1.35(111)$ is almost constant. Bottom right-hand side: Reciprocal lattice points of various α variants in the $(1\bar{1}0)$ bcc reciprocal plane. The Miller-Bravais notation has been used for the α peaks and different variants are indicated by indices. ○, ×, △, and □ indicate the structure factor s ($s^2 \propto 0,1,3,4$). Top right-hand side: Intensities of various α peaks in β-Zr. The open symbols correspond to measurements of β-Zr loaded with several at.% oxygen.

as a shearing of neighboring [111] chains relative to each other, while each chain itself remains rigid.[20] In β-Ti and β-Zr these effects are amplified by the particular d-band structure,[21] i.e., the charge density is highly anisotropic *along* the [111] chains. Finally, it is noted that the central energy as obtained from a damped oscillator fit of the measured phonon distribution in β-Zr $\hbar\omega_\omega = 7.6(5)$ meV which compares well with the results of the frozen phonon calculations of $\hbar\omega_\omega = 7.9$ meV.[21]

With regard to the often measured elastic diffuse scattering around the ω point in Zr alloys, though we could not find a superstructure peak at $\mathbf{Q}=1.33(111)$ in β-Ti or β-Zr, an extremely temperature- and sample-dependent elastic peak was found close by it at $\mathbf{Q}=1.28(111)$ (Fig. 2, left-hand side). The width of this peak never exceeded the instrumental resolution of ~ 0.01 rlu. This satellite intensity has already been reported by Stassis *et al.*,[18] but its origin has not yet been unambiguously discovered. Because of the high reactivity of the group-four metals with gaseous impurities, large amounts of oxygen can easily be absorbed in the sample at high temperatures. According to the phase diagram, an oxygen concentration of the order of 1 at.% leads to the coexistence of the α phase and the β phase at temperatures just above T_0. Taking into account that the observed α-phase lattice parameters a and c differ slightly from the α-phase lattice parameters a and c as calculated from the geometrical relationship between the bcc and hcp phase, the hcp Bragg peaks positions of the twelve variants can be calculated, e.g., the $(1\bar{2}.0)_{4,10}$ and $(2\bar{1}.0)_7$ hcp Bragg peaks appear at 1.28(111).[22] The assignment of the satellites to the *coherently* coexisting α structure within the β phase has unambiguously been proven by additional tests: (i) As indicated in Fig. 2 (bottom), hcp Bragg peaks are predicted for other points in $\mathbf{q}$ space which are definitely separated from ω positions and have been found exactly where expected, (ii) one sample was loaded *in situ* with several at.% of oxygen which resulted in a drastic increase of the hcp peak intensity and of its existence range in temperature (Fig. 2, top right-hand side), and (iii) samples with less than 0.1 at.% oxygen did not show α satellites in the β phase.

β-α transition: As shown in Fig. 3, the $T_1[\xi\xi 0]$ phonon branch with $[1\bar{1}0]$ polarization has a pronounced temperature dependence for both metals over the whole range of

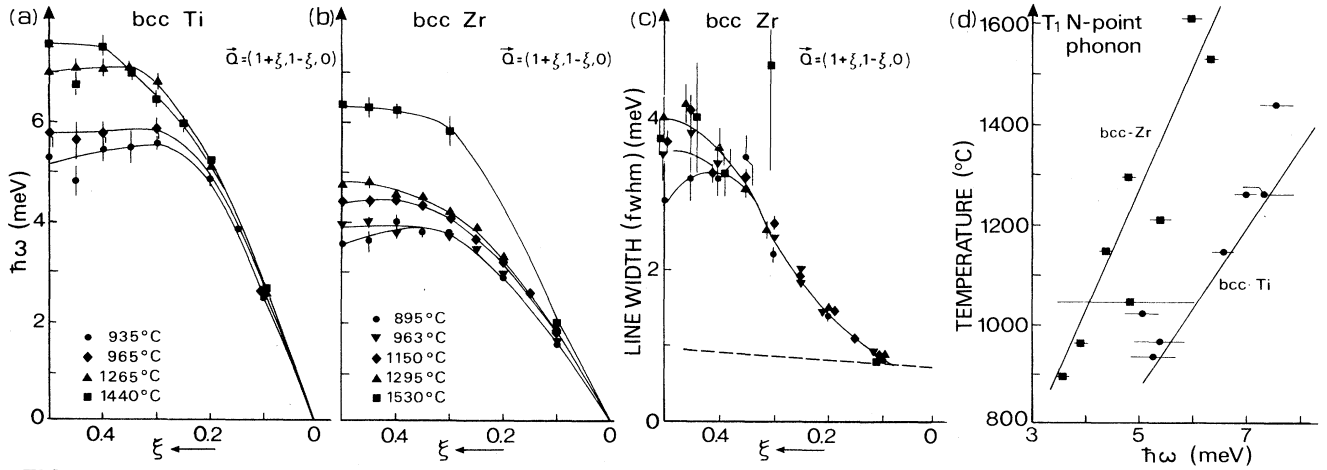

FIG. 3. Temperature dependence of the $T_{1[1\bar{1}0]}[\xi\xi 0]$ phonon branch in (a) β-Ti and (b) β-Zr. The measured spectra were fitted by a Gaussian and the peak positions are shown. (c) The corresponding line width for β-Zr are shown, the broken line indicates the instrumental resolution. (d) Temperature dependence of the $T_{1[1\bar{1}0]}\frac{1}{2}(110)$ phonon for β-Ti and β-Zr fitted simultaneously using the homology of the elements.

existence of the bcc phase. As stated above, it is just the N-point phonon of the $T_1[\xi\xi 0]$ branch which, from geometrical reasons, can be regarded as shuffling the bcc $\{110\}$ planes into the hcp stacking sequence. As with the ω point, the N-point phonon is also considerably damped. Approaching T_0 the N-point phonon softens but the actual phase transition clearly occurs at finite frequency. These observations may be compared to the results of frozen phonon calculations of the N-point phonon in Zr (Refs. 1 and 21) which have shown that the bcc phase is only stabilized by anharmonic contributions. For β-Zr at $T=1123\,^{\circ}\mathrm{C}$, these calculations yielded a phonon energy at the N point of $\hbar\omega_N=4.14(21)$ meV in surprisingly good agreement with our experimental result $\hbar\omega_N=4.39(7)$ for $T=1150\,^{\circ}\mathrm{C}$. The temperature dependence of $\hbar\omega_N$ calculated,[1] $d\hbar\omega_N/dT=8\times10^{-3}$ meV/K, and our measurements in Fig. 3(d), $d\hbar\omega_N/dT=4.1(4)\times10^{-3}$ meV/K, do not agree so well. However, considering the problems of such calculations we regard this discrepancy as not so severe.

A recent thermodynamic approach to the problem (expanding the free energy in terms of the dynamical displacements) has independently suggested that a further small softening of the relevant low-energy phonons is sufficient to produce a lower minimum of the free energy for the low-temperature phase.[3,5]

Elastic measurements on several samples of both metals around N points, in various Brillouin zones, and at various temperatures with a Ge(111) monochromator and analyzer in order to suppress $\lambda/2$ contaminations, showed to a high degree of precision *no intensity* which could be interpreted in terms of elastic precursors of the β-α transition.

In summary, we have shown experimentally that low-energy and strongly damped phonons in pure β-Ti and β-Zr produce the necessary displacements for the β-ω and β-α transition. The weakness of the bcc phase towards ω fluctuations is an inherent bcc property and is temperature independent. When the temperature is lowered to the β-α transition the corresponding T_1 N-point phonon, which is of low energy, decreases further but the transition itself occurs at finite frequency. The low energy, partly temperature-dependent and damped phonons confirm the theoretical considerations[1-6] of dynamical precursors of the MT's. In distinction to theory no long-living fluctuations into the α or ω phase, which should manifest itself as (quasi)elastic peaks, exist. We deduce a marked difference between pure systems and alloys: In alloys (quasi)elastic precursors of phase transitions appear,[7,19] whereas they are absent in pure systems.

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