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Reorientation relaxation of hydrogen in *C*16 intermetallic compounds

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In many intermetallic compounds of composition AB_2 having the tetragonal $C16$ ($CuAl_2$-type) structure, the component B has a much stronger chemical affinity to hydrogen than the component A. A general model of the anelastic reorientation relaxation of hydrogen in this type of alloys is proposed, which considers two possible, classical reorientation jumps of single hydrogen atoms involving one or both of the two types of B_4 tetrahedral sites existing in the $C16$ structure. The corresponding site and activation energies are calculated in terms of crystallographic parameters by applying a model of Richards [Phys. Rev. B **27**, 2059 (1983)], originally developed for amorphous metals, to the present case. Using crystallographic data from the literature, the dominant type of reorientation jump is predicted for almost two dozen $C16$ compounds. In addition, we also consider the response of the activation energy to various types of lattice distortions, which is different for the two suggested reorientation jumps; this makes an experimental distinction and test of the model possible. A first comparison with existing internal friction data on $CoZr_2$ and $NiZr_2$, especially with respect to the hydrogen concentration dependence of the peak temperatures, indicates a good qualitative agreement with the main predictions of the model.

I. INTRODUCTION

One of the classical mechanisms of anelasticity and internal friction (IF) in metals and alloys is the reorientation relaxation of interstitial impurities occupying sites that have a lower symmetry than the matrix and are thus orientationally distinguishable.[1] The experimentally observed effects are, however, characteristically different for hydrogen and for heavier interstitials (C,N,O), respectively.

The best-known relaxation mechanism is the Snoek relaxation, i.e., the anelastic relaxation produced by interstitial solutes in dilute solution in the body-centered-cubic (bcc) metals.[1] Since its first discovery for carbon in α-iron,[2] many experimental manifestations of this effect have been found; however, in spite of an intense search there is as yet no example of a hydrogen Snoek peak in a bcc metal.[3] Apparently a hydrogen reorientation relaxation in bcc metals requires the presence of trapping centers like other interstitial[4] or substitutional[5] solutes.

On the other hand, the most-observed case of a hydrogen reorientation relaxation is found in amorphous alloys, as reviewed by several authors,[6–9] but there is in turn no real equivalent to this effect due to heavier interstitials. Generalizing the term "Snoek relaxation," there is some disagreement in the literature whether the latter phenomenon in amorphous alloys[6] or the above-mentioned trapping effect in bcc metals[3] should be called the "Snoek-type" relaxation of hydrogen.

Compared to these two large groups of relaxation phenomena, the experimental basis for analogous single-atom reorientation relaxations in a crystalline matrix other than bcc is still very small; one example is known for oxygen in silicon.[1] With respect to hydrogen, some effects observed in hexagonal metals like Lu and Y have been attributed to H-H pairs.[10,11] Other hydrogen-induced internal friction peaks were found in the intermetallic compound Nb_3Sn (Ref. 12) and in the crystallization products of two Pd-base glasses,[6,13] but the atomistic relaxation mechanisms were not specified.

The first description of a H-induced internal friction peak in an intermetallic compound in terms of a specific mechanism was given recently for the equilibrium phase of $CoZr_2$ having a $C16$ ($CuAl_2$-type) structure.[14] As this phase was produced by crystallization of an amorphous sample, the development of the hydrogen IF spectrum could be followed for the whole crystallization sequence of this material. At low H concentrations, three IF peaks were attributed to reorientation jumps of single H atoms between Zr_4 tetrahedral sites embedded in the amorphous structure, in the grain boundaries of an intermediate, metastable nanocrystalline state[15] and in the final $C16$ crystal structure, respectively. Some similar, preliminary results were also obtained on a $Ni_{35}Zr_{65}$ alloy.[16] At almost the same time, some H-induced IF peaks were also found in disordered and ordered Pd_3Mn; they were attributed to reorientation jumps between certain pairs of interstitial sites surrounded by 4, 5, or 6 Pd atoms.[17]

In the present paper, a general model for the hydrogen reorientation relaxation in $C16$ compounds is derived from basic principles and worked out in detail for those AB_2 alloys with the $C16$ structure where the chemical affinity of hydrogen to the element B is higher than to A. Quantitative expressions for the relative probabilities of site occupation and specific atomic jumps and for the corresponding activation energies are obtained by applying a hopping model of Richards[18] (which was originally developed for amorphous metals) to this crystalline case. By using the known crystallographic parameters from the literature, numerical values are given for almost two dozen alloys. Finally, the main predictions of the model, including the response of the activation energy to different types of lattice distortions, are compared with the existing internal friction results on the $C16$ phases $CoZr_2$ and $NiZr_2$. A more detailed discussion of these results in the light of the present model will be given elsewhere.[19]

II. THE RELAXATION MODEL

A. Basic assumptions

The subject of the following considerations is the anelastic reorientation relaxation of single hydrogen atoms dissolved interstitially in the $C16$ ($CuAl_2$-type) crystal lattice of binary intermetallic compounds with composition AB_2. Direct H-H interactions and correlation effects between the individual jumps of the H atoms are neglected, i.e., we confine ourselves to low H concentrations. We assume classical hopping between equilibrium interstitial positions separated by saddle-point barriers and neglect any tunneling. The relaxation model is worked out for the case that the H atoms are occupying interstitial sites with only B atoms as nearest neighbors, so that the application of the model will be restricted essentially to those AB_2 alloys where hydrogen has a much higher chemical affinity to B than to A. This is the case, for instance, when A is a late and B is an early transition metal ("LTM-ETM" alloys).

This—rather severe—restriction to sites with a pure B-atom coordination shell finds some support from the present knowledge on hydrogen absorption in *amorphous* LTM-ETM alloys, the essential features of which have been expressed in general form by Harris, Curtin, and Tenhover.[20] According to their model, which appears to be well-confirmed on numerous systems, the H atoms are occupying tetrahedral sites in the amorphous structure. With increasing hydrogen concentration, the different possible types of tetrahedra are filled in the order B_4, AB_3, A_2B_2, etc., i.e., the site occupation is first of all determined by chemical interaction and only in a secondary manner by the effect of structural disorder. This view has also been supported by Kirchheim.[21]

Although this rather simple picture does not generally apply to *crystalline* alloys where the situation is surely more complex (e.g., due to additional contributions from configurational entropy and long-range, lattice-induced interactions[22]), the chemical environment of an interstitial site must play an important role also in that case, at least in addition to geometric criteria.[23] The question, however, whether the chemical interaction is so dominant as to justify the above assumptions, has to be answered in each individual case with respect to alloy composition, crystal structure, and H concentration range. The best conditions to fulfill these assumptions can certainly be expected for the case of low H concentrations, a large difference in the chemical affinities of hydrogen to A and to B, respectively, and a crystal structure that offers sufficiently large B_4 tetrahedral sites to the H atoms, which is the case for the $C16$ structure (see below).

B. Crystallographic description of the elementary reorientation jumps

The $C16$ ($CuAl_2$-type) crystal structure can be described as body-centered tetragonal, space group I4/mcm (No. 140), ideal composition AB_2, with 12 atoms/cell. Each unit cell contains four A atoms in the four a positions and eight B atoms in the eight h positions.[24,25] Possible interstitial sites in this structure are four types of tetrahedral sites: the 4 b and 16 l positions (both B_4 tetrahedra), the 32 m positions (AB_3 tetrahedra), and the 16 k positions (A_2B_2 tetrahedra).[26] Since in the known $C16$ compounds the B atoms are always larger than the A atoms,[25] the B_4 tetrahedra can generally be assumed to be larger than the AB_3 and A_2B_2 tetrahedra[27] and are thus favored also from the geometrical point of view. Accordingly, together with the above assumptions, we will consider in the following only the B_4 tetrahedra; we will also denote the 4 b sites as "type-1" and the 16 l sites as "type-2" tetrahedra, respectively.

For each interstitial site, the number of distinguishable configurations ("orientations") is given by the number of symmetry operations in the crystal class divided by the corresponding number in the point group of the site.[1] The tetragonal $C16$ crystal (point group 4/mmm) has 16 symmetry operations; the $4b$ (type 1) sites (point group $\bar{4}2m$) have also tetragonal symmetry but with only eight operations. The $16l$ (type 2) sites have monoclinic symmetry (point group m) with two operations.[26] Thus, there are two distinguishable orientations for the type-1 and eight for the type-2 sites.

The possibility of a reorientation relaxation, however, is not determined by these numbers but by the number n_t of possible orientations of the so-called λ tensor characterizing the "elastic dipole" of the defect; the symmetry of this tensor may be equal to or greater than that of the defect.[1] The value of n_t can be read from Table 8-2 (p. 185) in the book of Nowick and Berry;[1] it is one for the type-1 and four for the type-2 interstitial sites in the $C16$ lattice. Thus, the necessary condition for a reorientation relaxation ($n_t > 1$) is fulfilled if the type-2 sites can be occupied by the interstitial atoms.

The geometrical configuration of the A and B atoms in the $C16$ lattice as well as the positions of the type-1 and type-2 interstitial sites are shown in Figs. 1 and 2. There are four slightly different B-B nearest-neighbor distances (d_1,d_2,d_3,d_4); if the shorter distances d_1 and d_2 are considered preferentially, it is seen that the B atoms form two sets of mutually orthogonal planes [(110) and $(1\bar{1}0)$] with a dense packing of hexagons, with the A atoms situated in the remaining channels parallel to the c axis. Following Havinga, Damsma, and Hokkeling,[25] this kind of visualization of the $C16$ structure has been adopted in Fig. 1. The type-1 interstitial sites form a sublattice equivalent to that of the A atoms but displaced from the latter by a vector of $(a/2)$ (110); each type-1 site is surrounded tetrahedrally by four type-2 sites. These groups of five B_4 tetrahedral sites are arranged in chains along the c direction (like the A atoms), so that nearest-neighbor jumps of interstitials are possible between the type-1 and type-2 sites as well as between two type-2 sites, but not between two type-1 sites.

Figure 2 shows the geometry of the individual B_4 tetrahedra. It is obvious from this figure that the main axis of the elastic dipole of an interstitial atom in the center of a type-1 tetrahedron (with two edges of length d_1 and four edges of length d_3) must lie in the c direction. For a type-2 tetrahedron (with one d_1, one d_2, two d_3, and two d_4 edges), the dipolar axis lies in the (110) or in the $(1\bar{1}0)$ plane but inclined at a certain angle to the main crystallographic directions. It is easily seen from Figs. 1 and 2 that each group of one type-1 site with the four surrounding type-2 sites represents the five possible orientations of the elastic dipole, and that both types of nearest-neighbor jumps (1↔2 and 2↔2, see Fig. 3) involve a change in dipole orientation and hence a contribution to anelasticity.

The macroscopic anelastic response of a sample is essentially determined by a stress-induced redistribution of the population of interstitial atoms (e.g., hydrogen) between the four different orientations of the type-2 sites. The elementary process for such a redistribution is the change of an atom from one type-2 site to another. This is possible (1) by a direct nearest-neighbor jump between two type-2 sites (2→2), (2) by an indirect jump via a type 1 site (2→1→2, i.e., combination of two nearest-neighbor jumps[28]), or (3) by another type of indirect jump. This possibility requires at least a combination of three nearest-neighbor jumps including at least two additional AB_3 tetrahedral sites.

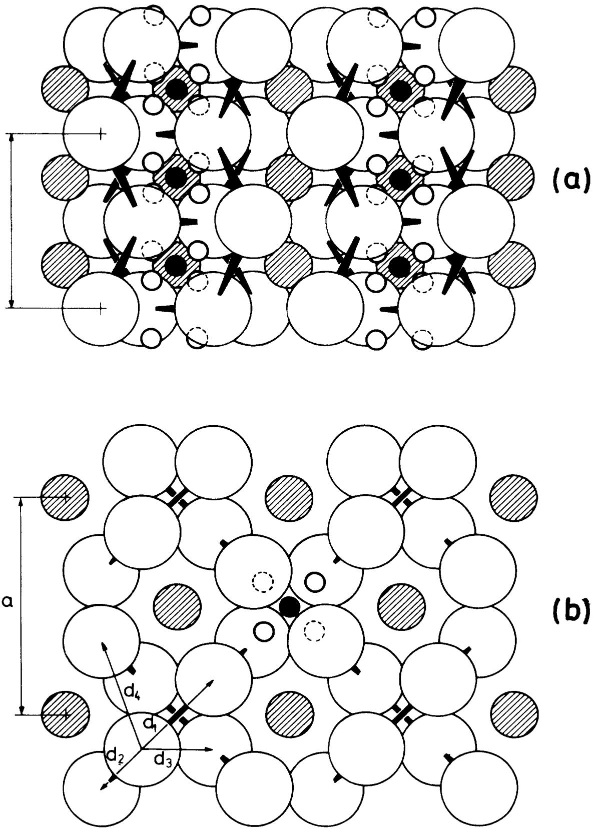

FIG. 1. The (100) and (001) projections of the $C16$ structure. The big, white atoms represent the element B, the smaller, shaded atoms A. The B atoms belonging to the same hexagon network have been graphically interlinked with each other (cf., Ref. 25). Indicated are also the positions of the B_4 tetrahedral interstitial sites: ●; type-1 site, ○; type-2 site (see text). (a) (100) projection, (b) (001) projection.

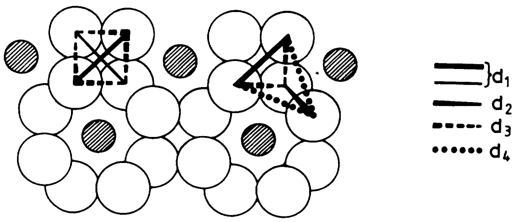

FIG. 2. The geometry of a type-1 (left) and type-2 (right) B_4 tetrahedron in the $C16$ structure [(001) projection].

In the present model, the first two of these possibilities (or, alternatively, the underlying nearest-neighbor jumps 2↔2 and 1↔2) are assumed as the elementary reorientation jumps of hydrogen atoms in $C16$ crystals; the third possibility is neglected. In the most general case, the mechanism of the reorientation relaxation would then be a combination of these two elementary jumps. However, contrary to long-range diffusion, which always requires more than one type of site and jump in the $C16$ lattice, we can expect in many cases that the short-range reorientation relaxation is dominated by only one type of jump. This question will now be addressed more closely by considering the dynamics of the reorientation jumps.

C. Site occupation and activation energies

The following considerations are largely based on the model of Richards,[18] which was originally developed for amorphous metals but which applies quite naturally also to the present case as long as it is sufficient to consider only the positions of the B atoms in the $C16$ lattice.

According to Richards,[18] the energy of a hydrogen atom in the equilibrium position at the center of a polyhedron of host atoms is determined by the sum of the lengths d_k of the polyhedron edges. This applies to the interstitial sites (tetrahedra, octahedra, or higher polyhedra) as well as to the saddle points (triangles). In that way the site energies U_i and the saddle-point energies U_{ij} $(i,j=1,2)$ for our type-1 and type-2 tetrahedral sites and

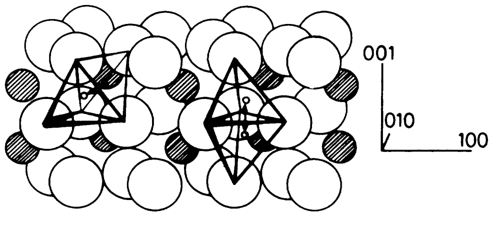

FIG. 3. The two possible types of nearest-neighbor jumps of interstitials between B_4 tetrahedral sites in the $C16$ lattice. Left: a jump between a type-1 and a type-2 site; right: a jump between two type-2 sites.

the saddle points in between, respectively, can be written as

$$U_i = U_{OE} + 6a_E - \frac{a_E}{d_0} \sum_{k=1}^{6} d_k^{(i)} \tag{1}$$

and

$$U_{ij} = U_{ji} = U_{OS} + 3a_S - \frac{a_S}{d_0} \sum_{k=1}^{3} d_k^{(ij)} , \tag{2}$$

where U_{OE} is the equilibrium site energy in the center of a regular tetrahedron and U_{OS} is the saddle-point energy in the center of a regular triangle, both with edge lengths d_0 (which may be, for instance, twice the atomic radius of the B atoms). The parameters a_S and a_E contain the hydrogen-metal forces at the saddle point and at the equilibrium point, respectively. The ratio a_S/a_E was estimated to $1.6 < a_S/a_E \lesssim 3$ for octahedral sites; experimental data on amorphous $Pd_{80}Si_{20}$ were best fitted for a_S/a_E at the lower limit, which is consistent with theory if some lattice relaxation around the H atoms is admitted.[18] For the present case of tetrahedral sites, the lower limit of a_S/a_E is $\sqrt{2}$;[18] hence, the value of $a_S/a_E = 1.5$ used in Sec. D (see below) seems reasonable.

The activation energy Δ_{ij} for hopping out of site i towards site j is

$$\Delta_{ij} = U_{ij} - U_i - \tfrac{3}{2}\hbar\omega_0 ; \tag{3}$$

the zero-point vibrational energy $\frac{3}{2}\hbar\omega_0$ of the hydrogen atom and, consequently, the "attempt frequency" ν_0 for the hopping rate $w_{ij} = \nu_0 \exp(-\Delta_{ij}/kT)$, are assumed to be the same at each site.[18] By inserting the appropriate interatomic distances d_1 to d_4 (see above) into Eqs. (1)–(3), we obtain the following expressions:

$$U_1 - U_2 = \frac{a_E}{d_0}[d_2 - d_1 + 2(d_4 - d_3)] , \tag{4}$$

$$\Delta_{22} = \frac{a_E}{d_0}\left[d_2 + 2d_3 - (d_1 + 2d_4)\left[\frac{a_S}{a_E} - 1\right]\right] + \text{const} , \tag{5}$$

$$\frac{\Delta_{12} + \Delta_{21}}{2} = \frac{a_E}{2d_0}\left[d_2 + 2d_4 + (d_1 + 2d_3)\left[3 - \frac{2a_S}{a_E}\right]\right] + \text{const} , \tag{6}$$

$$\Delta_{21} - \Delta_{22} = \frac{2a_S}{d_0}(d_4 - d_3) . \tag{7}$$

Thus, the difference of site energies $U_1 - U_2$ in Eq. (4) is proportional to a length $d_x := d_2 - d_1 + 2(d_4 - d_3)$, which is one of the parameters listed below in Table I. Neglecting other contributions like configurational entropy, the sites in the $C16$ lattice preferred for occupation by hydrogen would be expected to be the type-1 sites if $d_x < 0$ and the type-2 sites if $d_x > 0$. Nevertheless, in the temperature range of the reorientation relaxation a certain amount of H atoms will always occupy also the less favored sites because the difference $U_1 - U_2$ is normally much smaller than any of the activation barriers Δ_{ij}.

The most important parameter for the mechanism of the reorientation relaxation, however, is the difference $\Delta_{21} - \Delta_{22}$ in Eq. (7), which decides whether a H atom *in a type-2 site* is more likely to jump to a neighboring type-1 or type-2 site. In the present model, it is simply the difference of the interatomic distances d_3 and d_4 that determines whether the direct jump 2→2 (for $d_4 - d_3 > 0$) or the indirect jump 2→1→2 ($d_4 - d_3 < 0$) would be expected to be the dominating reorientation jump. It should be emphasized that the energy difference of Eq. (7), as a measure of the relative probability of the two processes, is not the same as the difference between the activation energies of the processes that are given by Eqs. (5) and (6).[29]

An almost complete list of the crystallographic parameters (including the distances d_1 to d_4) of the intermetallic compounds having the $C16$ structure can be found in the work of Havinga, Damsma, and Hokkeling.[25] For those compounds with a clear chemical affinity of hydrogen in favor of the B atoms—a necessary condition for the application of the present model—the resulting values of d_x and $d_4 - d_3$ are listed in Table I. In addition, the different AB_2 compounds are characterized by their c/a ratio and by the difference of the solution enthalpies of hydrogen in the pure components,[30] which may be taken as an approximate measure for the difference in the chemical interaction of hydrogen with the A and B

TABLE I. Hydrogen solution enthalpy differences $\Delta G_A^0 - \Delta G_B^0$ (Ref. 30) and crystallographic data (Ref. 25) suitable for predicting the preferred site occupation and reorientation jumps (see text) in several AB_2 compounds with $C16$ ($CuAl_2$-type) crystal structure.

Compound	$\Delta G_A^0 - \Delta G_B^0$ $(-G_B^0)$ (kJ/mol)	c/a	d_x (Å)	$d_4 - d_3$ (Å)
$CoSc_2$	130	0.881	−0.53	−0.25
$SiZr_2$	(60)	0.8016	0.50	0.15
$FeZr_2$	90	0.8764	−0.43	−0.22
$CoZr_2$	100	0.8671	−0.30	−0.17
$NiZr_2$	80	0.8124	0.19	0.05
$GaZr_2$	(60)	0.8105	0.68	0.17
$RhZr_2$	90	0.8628	−0.11	−0.12
$SiHf_2$	(40)	0.7914	0.58	0.19
$NiHf_2$	57	0.8200	0.19	0.04
$GeHf_2$	(40)	0.8022	0.60	0.17
$AlTh_2$	100	0.7695	0.61	0.25
$CuTh_2$	88	0.7941	0.41	0.15
$ZnTh_2$	(42)	0.7431	0.65	0.32
$GaTh_2$	(42)	0.7953	0.51	0.17
$GeTh_2$	(42)	0.8224	0.11	0.01
$PdTh_2$	30	0.8125	0.21	0.06
$AgTh_2$	110	0.7699	0.61	0.25
$InTh_2$	(42)	0.7829	0.85	0.28
$AuTh_2$	75	0.8026	0.51	0.15
$BeTa_2$	35	0.8136	0.29	0.07
$SiTa_2$	(40)	0.8208	0.18	0.03
$CoTa_2$	73	0.8125	0.34	0.09
$NiTa_2$	55	0.7843	0.47	0.17

atoms. Except for $PdTh_2$ and $BeTa_2$, the differences $\Delta G_A^0 - \Delta G_B^0$ always resulted from a positive ΔG_A^0 and a negative ΔG_B^0. In those cases where no ΔG_A^0 value was found due to a vanishing solubility of H in A, the value of $-\Delta G_B^0$ is given in parentheses as a lower limit for the appropriate enthalpy difference.

One important result from Table I is that d_x and $d_4 - d_3$ have always the same sign, i.e., the expected site occupation and relaxation mechanism are strongly correlated with each other. The sign is generally positive, except for $CoSc_2$, $FeZr_2$, $CoZr_2$, and $RhZr_2$. Hence, our model would predict a preferred occupation of the type 1 sites and the "indirect" reorientation jump $2 \rightarrow 1 \rightarrow 2$ only for these four alloys, and an occupation of the type 2 sites with dominating "direct" jumps in all other cases. No prediction can probably be made in the case of $GeTh_2$ where $d_4 - d_3$ is very close to zero.

D. Response to lattice distortions

An investigation of the influence of lattice distortions on the activation energies of the two suggested reorientation jumps [Eqs. (5) and (6)] can provide a chance to distinguish between these jumps by experiment and thus to test the predictions of the model. If the changes of all the independent crystallographic parameters of the $C16$ lattice [i.e., a, c, and x (Refs. 25 and 26)] due to an applied distortion are known, the response of the activation energies can be calculated quantitatively from the interatomic distances d_1 to d_4 by using the following equations:[31]

$$d_1^2 = 8a^2x^2 \ , \tag{8}$$

$$d_2^2 = \left[\frac{c}{2}\right]^2 + \frac{a^2}{2}(1-4x)^2 \ , \tag{9}$$

$$d_3^2 = \left[\frac{c}{2}\right]^2 + 4a^2x^2 \ , \tag{10}$$

$$d_4^2 = \left[\frac{a}{2}\right]^2 [1+(1-4x)^2] \ . \tag{11}$$

In many experimental cases, however, the change of x upon lattice distortion is not known as only the changes of a and c are detected. For this reason, we will only consider three special types of lattice distortion on a qualitative or, at most, semiquantitative level. We will also make a further simplification of Eqs. (5) and (6) by assuming a plausible value of $a_S/a_E = 1.5$ (see above):

$$\Delta_{22} = \frac{a_E}{d_0}[d_2 + 2d_3 - \tfrac{1}{2}(d_1 + 2d_4)] + \text{const} \ , \tag{12}$$

$$\Delta_{212} := \frac{\Delta_{12} + \Delta_{21}}{2} = \frac{a_E}{2d_0}(d_2 + 2d_4) + \text{const} \ . \tag{13}$$

(1) Volume expansion without change of c/a. If x remains unchanged, all the interatomic distances grow proportional to each other; the same holds for the activation energies Δ_{22} and Δ_{212} according to Eqs. (12) and (13). (This means that obviously the site energies are decreasing faster than the saddle-point energies.)

(2) c/a increase without volume change (i.e., decrease of a and increase of c). An exact prediction is not possible without knowing the change of x; the general tendency will be a decrease of d_1 and d_4 and an increase of d_2 and d_3. This will clearly cause an increase of Δ_{22}, whereas the change of Δ_{212} is unclear but probably small. In other words, the direct reorientation jump would be much more sensitive to such c/a changes than the indirect jump.

(3) Volume expansion with an increase of either a or c. If only a increases, d_1 and d_4 would increase much more than d_2 and d_3; this would cause a decrease of Δ_{22} and an increase of Δ_{212}. If only c increases, this influences d_2 and d_3; Δ_{22} would grow faster than Δ_{212}. However, a general prediction would be difficult as accompanying changes in x may result in a completely different behavior.

The two types of reorientation jumps should therefore be distinguishable by means of the responses of their activation energies to certain lattice distortions: The activation energy Δ_{22} of the direct jump would clearly increase with increasing ratio c/a, be it with or without a volume expansion. A decrease of c/a would lower Δ_{22}, quite pronounced at constant volume but probably still significantly when combined with a volume expansion. On the other hand, the activation energy Δ_{212} of the indirect jump seems rather insensitive to c/a changes at constant volume; it would always show an increase with volume expansion that would probably be more pronounced when combined with a decrease of c/a.

As hydrogen charging usually produces changes of lattice parameters of the type discussed here, an investigation of the dependence of the activation energy on the H concentration would be one possibility to test the predictions of the present model. Additional information can be expected from those alloys where it is possible to change c/a without varying the hydrogen content, as in the case of $CoZr_2$ (see below).

III. COMPARISON WITH EXPERIMENTS

As shown above, the relaxation model can be tested by studying the response of the activation energy to different types of lattice distortions. To do this quantitatively, however, the exact knowledge of the variation of all relevant crystallographic parameters (including x) is necessary for each investigated sample, which requires special experimental techniques and a comprehensive evaluation not only of the Bragg positions but also of the intensities, e.g., of x-ray-diffraction lines. As such a complete set of crystallographic information is not available for the samples used in the previous internal friction studies on the $C16$ phases $CoZr_2$ and $NiZr_2$,[14,16] it is not yet possible to perform such a quantitative test but only to compare the experimental results qualitatively with the main predictions of the model.

A detailed discussion of the existing experimental evidence in this context is beyond the scope of this paper and will be given elsewhere.[19] In what follows, we recall briefly the reorientation jumps underlying the observed internal friction peaks in $CoZr_2$ and $NiZr_2$ according to our model, and then compare the measured peak temperatures (e.g., at different hydrogen concentrations) with the changes of activation energy expected.

In Table I, the sign of the parameters d_x and $d_4 - d_3$ is negative for $CoZr_2$ and positive for $NiZr_2$. As already pointed out above, this implies a preferred occupation of the type 1 interstitial sites with hydrogen and the indirect reorientation jump $2 \rightarrow 1 \rightarrow 2$ as the dominant processes in $CoZr_2$, whereas in $NiZr_2$ we expect mainly an occupation of the type 2 sites—which is indeed confirmed by neutron diffraction[32]—and the direct jump $2 \rightarrow 2$. These processes define the mechanisms underlying the observed internal friction peaks in $CoZr_2$ [Fig. 4(a)] and $NiZr_2$ [Fig. 4(b)], respectively. Thus, the present model has answered the question of the dominant elementary reorientation jump, which was left open in the more heuristic and preliminary explanations given in our earlier papers.[14,16]

However, as the value of $d_4 - d_3$ for $NiZr_2$ in Table I is rather close to zero, a participation of the second type of jump is more likely in $NiZr_2$ than in $CoZr_2$. Recent results have indeed shown the development of a second internal friction peak in $NiZr_2$ under certain conditions; this particular case is discussed elsewhere.[19]

In the range of hydrogen concentrations (of, at most, some atomic percent) considered here, we expect a volume expansion combined with a decrease of c/a both in $CoZr_2$ and $NiZr_2$ when the H content of the sample is raised.[33] As shown above, this kind of lattice distortion would result in an increase of the activation energy Δ_{212} for the indirect jump and in a decrease of Δ_{22} for the direct jump. Hence, our model predicts an increase of the activation energy of the reorientation relaxation of H in $CoZr_2$ and a decrease in $NiZr_2$, respectively, with increasing hydrogen concentration.

With respect to the shape of the resulting internal friction peaks, in a perfect $C16$ crystal a single relaxation time and hence a Debye peak[1] would be expected for each elementary reorientation jump showing a single activation energy and a constant attempt frequency, as suggested by the model. In contrast, the internal friction peaks shown in Fig. 4 are distinctly broader.[34] As the most probable explanation for this disagreement, we consider the fact that the samples used in these cases (produced by crystallization of amorphous $Co_{33}Zr_{67}$ and $Ni_{35}Zr_{65}$ ribbons, respectively) have a very fine-grained microstructure, possibly with internal stresses, and are thus far from being perfect crystals. In addition, possible gradients in hydrogen concentration would also produce variations of lattice parameters, and hence of activation energy and relaxation time within the sample.

For this reason, we do not consider here the full shape of an internal friction peak but only the position of its maximum ("peak temperature") defining the most probable relaxation time via an Arrhenius relationship.[1] According to the above assumption on the attempt frequency justified in the paper of Richards,[18] we neglect variations of the pre-exponential factor τ_0 and thus consider the peak temperature (at constant vibration frequency) as a direct measure of the activation energy Q_a. [Independent data on Q_a and τ_0 are only available in case 1 in Fig. 4(a), with $Q_a = 0.41 \pm 0.06$ eV and $\tau_0 = 10^{-12.6 \pm 1.2}$ s.[14]] With these assumptions, Fig. 4 shows that on increasing the hydrogen content, the activation energy is slightly increasing in $CoZr_2$ but decreasing the $NiZr_2$—exactly what is predicted by the model.

In addition to this qualitative confirmation of the model by the hydrogen concentration dependence, it would be interesting to test also the influence of the other types of lattice distortions considered at the end of Sec. II. Fortunately, the alloy $CoZr_2$ offers here a special chance: If the $C16$ phase is produced by crystallization from the amorphous state, it is possible to change the c/a ratio, at

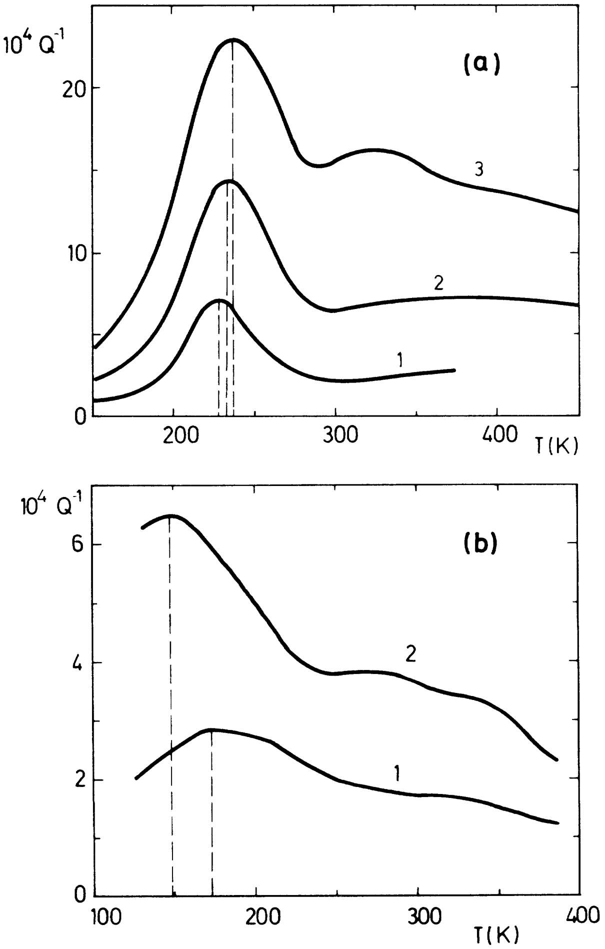

FIG. 4. The H-induced internal friction peaks in the $C16$ phases $CoZr_2$ and $NiZr_2$ (after Ref. 16), as measured as a function of temperature at a frequency of about 400 Hz with the vibrating-reed technique (with $Q^{-1} = \Delta W / 2\pi W$, relative energy loss per cycle). In both examples shown, a single sample was crystallized into the $C16$ structure from the amorphous state and then stepwise charged with H_2 gas (pressure 50–100 kPa) to obtain different, increasing hydrogen concentrations. (a) $CoZr_2$, from initially amorphous $Co_{33}Zr_{67}$ (curve 1: 0.3 at % H, without charging; curve 2: charged for 35 h at 371 K; curve 3: charged for additional 18 h at 468 K); (b) $NiZr_2$, from initially amorphous $Ni_{35}Zr_{65}$ (curve 1: without charging; curve 2: charged for 11 h at 468 K).

constant H concentration, by a simple thermal treatment. No significant shift of the internal friction peak after such a treatment is observed. This is in general agreement with the predicted insensitivity of the indirect reorientation jump to c/a changes.[35]

A principal limitation of the quantitative significance of the proposed relaxation model lies in the fact that like in the model of Richards,[18] local displacements of the metal atoms around a H atom due to lattice relaxation have not been taken into account quantitatively. This makes a direct comparison between experimental data on different $C16$ phases more difficult; for this reason, we do not discuss here the observed peak temperatures in $CoZr_2$ and $NiZr_2$ relative to each other. More internal friction data also on other $C16$ phases, together with a better knowledge of the actual crystallographic parameters, will be required to obtain a better and more quantitative picture of the validity and limitations of the proposed relaxation model.

IV. CONCLUSIONS

In the above relaxation model (Sec. II), a microscopic mechanism of a single-atom reorientation relaxation of interstitials in a specific intermetallic structure—the tetragonal $C16$ structure—has been combined, for the first time, with the results of a first-principles calculation of activation energies for impurity hopping.[18] The resulting quantitative relationships between the activation energies and crystallographic parameters were used to predict the dominant atomic jump expected in 23 $C16$ compounds and the response of the activation energy to different types of lattice distortions. As discussed in detail elsewhere,[19] these predictions are qualitatively consistent with the few existing experimental data on hydrogen-induced internal friction in $C16$ compounds; however, more (and more specific) experiments are clearly needed to arrive at a quantitative test of the model.

The present work was largely stimulated by the progress made on amorphous alloys during the past decade, insofar as both the underlying activation energy calculations[18] and the internal friction results originally came out of that field. The resulting model may be considered as a new approach to the field of mechanical relaxation of interstitials (especially hydrogen) in intermetallic compounds; such an approach can, in principle, be applied also to other types of intermetallic structures.

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[28] This does not necessarily mean that the two partial jumps $2 \rightarrow 1$ and $1 \rightarrow 2$ are made by the same atom, which is indeed not very likely especially in those cases when the interstitial atoms are preferably occupying the type-1 sites, as discussed further below.

[29] The identity of Eq. (6) with the activation energy of the indirect jump $2 \rightarrow 1 \rightarrow 2$ follows from the corresponding rate equations if the net jumping rates $1 \rightarrow 2$ and $2 \rightarrow 1$ are set equal, i.e., if it is assumed that the stress-induced redistribution of the interstitials between the type-2 sites occurs without changing the population in the type-1 sites. This assumption seems justified from the crystallographic considerations made above.

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[33] In the case of $NiZr_2$, the c/a decrease was measured by neutron diffraction (Ref. 29). For $CoZr_2$ we do not know such data, but a c/a decrease is here also expected from the geometry of the type-1 interstitial site (Fig. 2), which is elongated in the (001) direction compared to a regular tetrahedron.

[34] A direct comparison of the peak in $CoZr_2$ with a Debye peak has been given in Ref. 14.

[35] A more detailed treatment of this point can also be found in Ref. 19.