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MECHANICAL RELAXATION OF SUBSTITUTIONAL-INTERSTITIAL (TETRAHEDRAL) ATOM COMPLEXES IN THE bcc LATTICE

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Abstract- The relaxation of a substitutional-tetrahedral interstitial atom pair in the bcc lattice is studied theoretically. Three relaxation modes can be excited mechanically, one by a tensile stress along the <111> direction and the other two by the <100> direction. The kinetics of the <100> relaxation are examined in detail. Experimental results of internal friction studies on Nb-Ti-H and V-Ti-H alloys are discussed in the light of the present analysis.

1. Introduction.- In internal friction studies of Nb-Ti-H [1,2] and V-Ti-H [3] alloys, new relaxation peaks are found which are considered to be due to Ti-H complexes. A similar effect has also been found by Kronmüller and Vetter [4] in magnetic after-effect measurements on Fe-Ti-H and Fe-Ti-D alloys. Hydrogen atoms are usually considered to occupy tetrahedral interstices in various bcc metals. In the present paper, therefore, we discuss the relaxation process of a substitutional atom - a tetrahedral interstitial atom (s-i) pair in the bcc lattice; the relaxation of the s-i(octahedral) pair has been previously discussed by one of the present authors [5].

2. Classification of relaxation modes.- A general theory of the relaxation of point defects is discussed in detail by Nowick and Berry [6]. Although the mechanical relaxation modes associated with paired point defects in cubic lattices have been derived and tabulated by Chang [7], the relaxation of the s-i (tetrahedral) pair has not been treated in his paper.

The s-i (tetrahedral) pair in the bcc lattice (Fig.1) is a <100> monoclinic defect. Consider the defect orientation in the figure. The principal axes (x' and z') of the λ tensor are inclined with respect to the crystal axes: (x and z). The components of the tensor, λ_{ij}, in the crystal coordinate system are given by

\begin{align*}
\lambda_{11} &= \lambda_{1} \cos^{2} \theta + \lambda_{3} \sin^{2} \theta, \\
\lambda_{22} &= \lambda_{2}, \\
\lambda_{33} &= \lambda_{1} \sin^{2} \theta + \lambda_{3} \cos^{2} \theta, \\
\lambda_{12} &= \lambda_{21} = \lambda_{23} = \lambda_{32} = 0, \\
\lambda_{31} &= \lambda_{13} = (\lambda_{1} - \lambda_{3}) \sin \theta \cos \theta,
\end{align*}
where \( \lambda_i \) are the principal values.

By the standard method (see, e.g. [6]), the relaxation modes for the pair can be derived and are listed in Table 1. (we omitted ungerade modes.) Here we assumed that (1) the s. atom is immobile, (2) i. atoms are confined to 24 interstices around s. atom, and (3) the i. atom jump only between nearest neighbour sites with a frequency \( \nu \) within one \{100\}, and with \( \nu' \) from one \{100\} to a neighbouring \{100\} plane, as shown in Fig.2. The numbering of sites is also indicated in this figure. Among the five types of relaxation in the table, only two of them, \( T_{2g} \) and \( E_g \), are excitable.

3. Relaxation process under uniaxial stresses.- All the essential information of the relaxation is given in Table 1, the derivation of which is based upon a group-theoretical consideration. In order to visualize the relaxation process it seems worthwhile to consider the problem from a somewhat different point of view; we shall examine the rearrangement of i. atoms under the application of the unidirectional stresses: \(<111>\) and \(<100>\) tensile stresses.

3.1. The \(<111>\) case.- Under the \(<111>\) tensile stress, the interstices are classified into two groups of sites, 1 and 2 as shown in Fig.3a; in each group the probability of occupation of sites by i. atoms is the same. We define the occupation probability, \( n_1 \) and \( n_2 \), that the i. atom occupies any of sites in group 1 or 2. The rate equations for \( n_1 \) and \( n_2 \) are

\[
\frac{\dot{n}_1}{n_1} = -\nu (n_1 - n_2), \quad \frac{\dot{n}_2}{n_2} = -\nu (n_2 - n_1). \tag{1}
\]

These are expressed by a single equation for \( (n_1 - n_2) \), and the relaxation time is

\[
\tau = (2\nu)^{-1}. \tag{2}
\]

The relaxation of the compliance is

\[
\delta E_{<111>}^{-1} = \left( 4 C_0 v_0 / g k T \right) \lambda_{13}^2, \tag{3}
\]

where \( C_0 \) is the mole concentration of s-i pairs and \( v_0 \) the atomic volume of the matrix atom.

In the absence of substitutional impurity atoms, the symmetry of tetrahedral interstitials is tetragonal \( (\theta=0, \lambda_{13}=0) \), and no relaxation occurs for the \(<111>\) tensile stress.

3.2. The \(<100>\) case.- Under the \(<100>\) tensile stress, the interstices are classified into three groups, 1, 2 and 3, as shown in Fig.3b; we
define the occupation probabilities $n_1$, $n_2$ and $n_3$, similarly to the $<$111$>$ case. The rate equations are

$$\begin{align*}
\dot{n}_1 &= -\nu' n_1 + \nu n_2 , \\
\dot{n}_2 &= - (2\nu + \nu') n_2 + 2\nu n_3 + \nu' n_1 , \\
\dot{n}_3 &= - 2\nu n_3 + 2\nu n_2 .
\end{align*}$$

These can be solved in a straightforward way, and we only list important quantities below. The relaxation times $\tau_+$ and $\tau_-$ are

$$\tau_\pm^{-1} = \nu' + 2\nu \pm D , \quad D = \sqrt{(\nu'^2 + 4\nu^2 - 2\nu\nu')} .
$$

The normal coordinates are

$$\nu' n_1 - (2\nu \pm D) n_3 + (2\nu - \nu' \pm D) n_2 .
$$

The relaxation of the compliance for the two modes is

$$\delta E_{<100>}^{-1} = \frac{C_0 v_0}{18kT} \frac{2D \tau(4\nu - \nu')}{D\nu'^2} \times \left[ \nu'(\lambda_{33} - \lambda_{22}) + (2\nu \pm D)(\lambda_{22} - \lambda_{33}) \right]^2 .
$$

The sum of the two is independent of $\nu$ and $\nu'$;

$$\delta E_{<100>}^{-1} = \frac{C_0 v_0}{9kT} \left[ (\lambda_{11} - \lambda_{22})^2 + (\lambda_{22} - \lambda_{33})^2 + (\lambda_{33} - \lambda_{11})^2 \right] .
$$

4. Numerical example.- The relaxation times for the three modes, one for the $<$111$>$ case and two for the $<$100$>$ case are shown in Fig.4 as a function of the ratio of jump frequencies, $\nu'/\nu$. As mentioned before, the relaxation strength for the $<$111$>$ case is considered to be rather small. Hereafter, we only discuss the $<$100$>$ case.

For the sake of brevity, we assume that $\lambda_{22} = \lambda_{33}$; this relation exactly holds for free hydrogen atoms in the matrix. The relaxation spectrum as a function of the angular frequency $\omega$ can be written, from eqs. (5) and (7) as

$$S(\omega) = \left( 1 + \frac{\nu' + 2\nu}{2D} \right) \frac{\omega \tau_+}{1 + (\omega \tau_+)^2} + \left( 1 - \frac{\nu' + 2\nu}{2D} \right) \frac{\omega \tau_-}{1 + (\omega \tau_-)^2} .
$$

The spectrum changes sensitively depending upon the ratio, $\nu'/\nu$.

Figure 5 shows the spectra $S(\omega)$ for various values of $\nu'/\nu$. (Here, $\omega_0$ is taken as $\omega_0 \tau_+ = 1$ for $\nu'/\nu = 1$.) At $\nu'/\nu = 2$, the peak is the highest. By increasing or decreasing the ratio, $\nu'/\nu$, the peak decreases its height and broadens, and eventually splits into two peaks.

The relaxation strengths for the two components corresponding to $\tau_+$ and $\tau_-$ are shown in Fig.4. The peak for $\tau_+$ is always higher than that for $\tau_-$. The strength ratio is 3 for extreme values
At $\nu'/\nu = 2$, the relaxation strength for the $\tau_-$ peak is zero, and the spectrum is of a single relaxation time.

5. Comparison with experimental results.- The relaxation peaks observed in Nb-Ti-H [2], and V-Ti-H [3] alloys have been interpreted as due to Ti-H complexes. The peaks are broader than those expected for the single relaxation process. In the previous analysis [2], it has been suggested that the broadness may be due to the presence of titanium-hydrogen complexes with different number of hydrogen atoms: Ti-H, Ti-H$_2$, ... The present analysis suggests that the broadness could be, at least partly, of an intrinsic nature; even for a simple complex Ti-H, there exist three relaxation processes.

In the previous paper [2], two possibilities have been suggested for the origin of subsidiary peaks at a lower temperature; (1) the reorientation of hydrogen atoms around Ti-Ti complexes, (2) a satellite arising also from Ti-H complexes which are responsible for the main peak. The present analysis shows that the satellite does exist if two jump frequencies $\nu$ and $\nu'$, are considerably different. With the assumption that $\lambda_{22} = \lambda_{33}$, however, the low temperature peak always has a larger relaxation strength than the higher temperature peak. Experimentally, the higher temperature peak is much larger for Nb-Ti-H and V-Ti-H alloys. Therefore, it seems reasonable to interpret the subsidiary peak as arising from Ti-H complexes. A different conclusion may be derived if a different anisotropy is assumed for the $\lambda$ tensor of the defect pair.

The present calculation has been made on the assumption that hydrogen atoms are confined to 24 interstices around a titanium atom, and are not allowed to jump out to outside sites. A more realistic treatment should consider the possibility of outward jumps.

References
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3. S. Tanaka and M. Koiwa; this issue.
5. M. Koiwa; Phil. Mag., 24, 81 (1971); 24, 107 (1971); 24, 539 (1971); 24, 799 (1971); 25, 701 (1972).
Table 1: Relaxation modes of a substitutional-tetrahedral interstitial atom pair in the bcc lattice

<table>
<thead>
<tr>
<th>Representation</th>
<th>Type of Relaxation mode</th>
<th>normal coordinate*</th>
<th>relaxation frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{1g}</td>
<td>Equilibrium</td>
<td>s\textsubscript{x} + s\textsubscript{y} + s\textsubscript{z}</td>
<td>0</td>
</tr>
<tr>
<td>A\textsubscript{2g}</td>
<td>Inactive</td>
<td>p\textsubscript{x} + p\textsubscript{y} + p\textsubscript{z}</td>
<td>4\nu + 2\nu'</td>
</tr>
<tr>
<td>T\textsubscript{1g} (3)</td>
<td>Inactive</td>
<td>cy\textsubscript{1} - cy\textsubscript{3} - cz\textsubscript{2} + cz\textsubscript{4}</td>
<td>2\nu + 2\nu'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cz\textsubscript{1} - cz\textsubscript{3} - cx\textsubscript{2} + cx\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>cx\textsubscript{1} - cx\textsubscript{3} - cy\textsubscript{2} + cy\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>T\textsubscript{2g} (3)</td>
<td>&lt;111&gt; tensile stress</td>
<td>eq. (7)</td>
<td>eq. (5)</td>
</tr>
</tbody>
</table>

\* s\textsubscript{j} = c\textsubscript{j1} + c\textsubscript{j2} + c\textsubscript{j3} + c\textsubscript{j4}, \quad p\textsubscript{j} = c\textsubscript{j1} - c\textsubscript{j2} + c\textsubscript{j3} - c\textsubscript{j4}

c\textsubscript{j1} are the occupation probabilities of j\textsubscript{i} sites.

For the numbering of sites, see Fig. 2.

Fig. 1: The substitutional-tetrahedral interstitial atom pair in the bcc lattice.
O: Metal atoms
●: A substitutional atom
○: A tetrahedral interstitial atom

Fig. 2: The numbering of tetrahedral interstices.
Fig. 3: Classification of tetrahedral interstices under the application of uniaxial stresses:
a) the ⟨111⟩ tensile stress.
b) the ⟨100⟩ tensile stress.
The interstices on each ring have the same occupation probability.

Fig. 4: Relaxation times for the three relaxational modes, and the relaxation strengths for the two ⟨100⟩ relaxations (see eq. (g)).

Fig. 5: Spectra of the ⟨100⟩ relaxation for various values of ν'/ν.