INTERACTIONS - DÉFAUTS PONCTUELS - RÉSEAUAELASTIC EFFECTS DUE TO POINT DEFECTS IN SOLIDS

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ANELASTIC EFFECTS DUE TO POINT DEFECTS IN SOLIDS

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Résumé. — Les défauts ponctuels présents dans des solides, sont la cause d’effets anélastiques qui se manifestent par des pics de relaxation, de frottement intérieur. L’effet des atomes dissous interstitiels et substitutionnels, des lacunes et leurs interactions complexes, sur les caractéristiques de tels pics, est revisé. Les modèles qui expliquent les différents pics de relaxation sont examinés sous forme de la compréhension actuelle de l’ordre par des tensions de défauts ponctuels.

Abstract. — Point defects present in solids cause anelastic effects which manifest themselves as internal friction, relaxation peaks. The characteristics of such peaks due to interstitial and substitutional solute atoms, vacancies, self-interstitials, and their interacting combinations are reviewed. Models of the relaxation processes are discussed in terms of the present understanding of the stress-induced ordering of the point defects.

1. Introduction. — The point defects considered in this review are: (a) interstitial solute atoms, (b) substitutional solute atoms, (c) vacancies and (d) self-interstitials. The first two defects are known as extrinsic and the latter two as intrinsic lattice defects. The main interest of this paper is the fact that most point defects, and certain interacting combinations of the elementary defects, produce the property of anelasticity. This term was coined by Zener [1] to describe a particular type of imperfect elastic behaviour exhibited by solids.

Solids containing point defects exhibit anelastic behaviour (of which internal friction is one manifestation) through a process known as stress-induced ordering. This process involves the change with time of an equilibrium configuration of defects in the absence of stress to a new and unique state of order under the influence of an applied stress. When the stress is removed the change is reversed, and with time the original state of order is restored. In the case of an oscillating applied stress there is a phase lag between the stress and strain which results in energy loss known as internal friction. The internal friction passes through a maximum when the applied frequency is uniquely related to the relaxation time of the process [1-5].

The formal theory of the anelastic behaviour will not be dealt with in this paper for two reasons. Firstly, a number of excellent reviews [1-5] are available, and secondly, such treatment is outside the scope of the present review.

The application of internal friction measurements to diffusion studies in metals has also received extensive treatment elsewhere [6, 7]. The object of this paper is to review the characteristics of the internal friction peaks due to stress-induced ordering of point defects and their interacting combinations in solids, and the relaxation models causing the peaks. In some cases, notably the stress-induced ordering of interstitial solute atoms in BCC transition metals (the Snoek peak), the model of the relaxing unit is comparatively easy to visualise when considered under the influence of an uniaxial stress. This is, however, not so for more complex stresses or other lattice structures. During the last few years attempts have therefore been made to produce a unified theory for the mechanical relaxation phenomena due to point defects, such as (a) the elastic dipole formalism [5, 8-10], (b) the crystallographic method [11-15] and (c) the use of group theory methods [16-19].

In the first part of the paper the Snoek relaxations are reviewed in detail and in the subsequent three parts the Zener relaxation, relaxation processes associated with interacting combinations of unlike extrinsic defects and relaxations associated with intrinsic defects are reviewed in a more factual manner. An attempt is made to give a fairly comprehensive treatment of each group of the relaxation processes. In some cases, however, where the inferences are not conclusive, because of conflicting interpretations and/or lack of critical results, the presentation is restricted to stating observations.

2. The Snoek relaxation peak. — In 1939 Snoek [20] showed that internal friction peaks in iron were due to the presence of carbon and nitrogen as interstitial solutes. Two years later he [21] proposed that the internal friction peaks (known as Snoek peaks) were due to stress-induced ordering of interstitial carbon and nitrogen atoms, occupying the octahedral $(4, 0, 0)$ sites.

From Snoek’s theory it is to be expected that the relaxation effect in BCC metals containing interstitial solute atoms will be anisotropic, and the magnitude of the effect will vary with the direction in which the stress is applied. Thus, if a tensile stress is applied along $<111>$ direction, no interstitial sites become preferred, as all the tetragonal axes are equally inclined toward the tensile axis. This was verified experimentally by Dijkstra [22] and more recently by Lord and Beshers [23] using single crystals of iron, and Hoffman and Wert [24] using single crystals of niobium.

2.1 The Snoek Peak in BCC Transition Metals. — Since the relaxation peaks in alpha-iron, a BCC metal, have been shown to be due to the stress-induced ordering of interstitial carbon and nitrogen, it was anticipated that the BCC transition metals containing these elements should show the same effect. Investigations by many workers confirmed this expectation and the existence of the Snoek relaxation peaks were reported in the Group VA metals, tantalum [25-33], niobium [27, 28, 32, 34-38] and vanadium [32, 39-43] and the Group
VIA metals chromium [45-47], molybdenum [48, 49] and tungsten [50-53]. Furthermore, it has been observed that in the Group VA metals, besides nitrogen and carbon, oxygen too can cause stress-induced ordering.

2.1.2 The Group VIA Metals. — The study of the behaviour of interstitial atoms in the Group VIA metals using the internal friction method has not been as extensive as in the case of iron and the Group VA metals. Furthermore, the results so far obtained are less self-consistent as compared with the above metals. Bungardt and Preisendanz [45] observed a peak at 180 \(^\circ\)C (1 Hz) in nitrogen charged chromium, which they interpreted in terms of stress-induced ordering of nitrogen. Subsequently, De Morton [46] reported a peak at 160 \(^\circ\)C (0.92 Hz) in a chromium-nitrogen alloy. The associated activation energy of the relaxation process causing the peak was found to be 24.3 kcal.mol\(^{-1}\). This value agreed with the activation energy for the diffusion of nitrogen in chromium determined by the elastic after-effect method [46]. De Morton also observed that the nitrogen Snoek peak was steeper on the high temperature side, and showed that this effect was caused by extensive precipitation of nitrogen from free solid solution during the internal friction measurements. More recently Klein and Clauer [47] re-investigated the nitrogen Snoek peak in chromium in greater detail, studying the effect of nitrogen concentration and nitrogen precipitation on the height and shape of the peak. The associated activation energy of the relaxation process determined by Klein and Clauer is 20.5 kcal.mol\(^{-1}\), which is lower than that found by De Morton [46] by 3.8 kcal.mol\(^{-1}\). This difference, as pointed out by Klein and Clauer, cannot be accounted for either by the effect of precipitation of nitrogen on the peak temperature of the peak nor by the difference in purity of the materials used. Comparing the three reported peak temperatures [45-47] it appears that the nitrogen Snoek peak in chromium occurs at about 160 \(^\circ\)C (1 Hz).

Investigating the internal friction of high purity molybdenum Maringer and Schwoppe [48] observed peaks at about 230\(^\circ\) to 290\(^\circ\)C and 310\(^\circ\) to 370\(^\circ\)C (1 Hz). These peaks they suggested to be the carbon and nitrogen Snoek peaks respectively. More recently Schnitzel [49] re-investigated the carbon peak in single crystals of molybdenum and found that (a) it occurred at 200\(^\circ\) to 225 \(^\circ\)C (1 Hz), (b) it was too broad for single relaxation time, (c) its height was unaffected by carburising beyond 0.0034 wt % carbon and (d) carbon was precipitating during measurements. Using the Wert and Marx [79] relationship Schnitzel deduced an approximate value of the associated activation energy of the relaxation process of the 200-225 \(^\circ\)C peak as being 30 to 32 kcal.mol\(^{-1}\).

In tungsten a peak occurring at about 400 \(^\circ\)C (1 Hz) was also reported and shown to be a Snoek peak due to carbon [50-53]. The associated activation energy of the relaxation process causing the peak was reported as being 45-47 kcal.mol\(^{-1}\) [51-53] which is slightly lower than that (51 kcal.mol\(^{-1}\)) for the diffusion of carbon in tungsten [80]. The height of the peak also decreased during measurements, and varied with...

### Table I

<table>
<thead>
<tr>
<th>System</th>
<th>Activation Energy (cal.mol(^{-1}))</th>
<th>Peak Temperature at 1 Hz</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-O</td>
<td>258 820</td>
<td>149</td>
<td>25, 26, 28, 30, 32, 33</td>
</tr>
<tr>
<td>Ta-N</td>
<td>358 000</td>
<td>344</td>
<td>25, 28, 30, 32, 33</td>
</tr>
<tr>
<td>Ta-C</td>
<td>38750</td>
<td>351</td>
<td>31-33</td>
</tr>
<tr>
<td>Nb-O</td>
<td>26700</td>
<td>156</td>
<td>32, 37, 38</td>
</tr>
<tr>
<td>Nb-N</td>
<td>34900</td>
<td>387</td>
<td>32, 37, 38</td>
</tr>
<tr>
<td>Nb-C</td>
<td>33150</td>
<td>259</td>
<td>32, 37, 38</td>
</tr>
<tr>
<td>V-O</td>
<td>28920</td>
<td>183</td>
<td>32, 39-44</td>
</tr>
<tr>
<td>V-N</td>
<td>34600</td>
<td>271</td>
<td>32, 39-44</td>
</tr>
<tr>
<td>V-C</td>
<td>27300</td>
<td>170</td>
<td>32, 41</td>
</tr>
<tr>
<td>Fe-N</td>
<td>18300</td>
<td>22</td>
<td>32, 41</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>202 500</td>
<td>36</td>
<td>32, 41</td>
</tr>
<tr>
<td>Cr-N</td>
<td>24300</td>
<td>161</td>
<td>32, 41</td>
</tr>
<tr>
<td>Mo-C</td>
<td>30000-32000</td>
<td>200-225</td>
<td>47</td>
</tr>
<tr>
<td>W-C</td>
<td>46000</td>
<td>410</td>
<td>51-53</td>
</tr>
</tbody>
</table>
treatments affecting the amount of carbon retained in free solid solution.

Summarising the Snoek peaks in the Group VIA metals it can be stated that the peaks due to nitrogen in chromium and to carbon in tungsten are reasonably well understood; whereas the carbon peak in molybdenum is still uncertain. The main difficulty in studying the Snoek peaks in these metals is the very low solid solubility of the interstitial solute atoms, resulting in very small peaks. In most cases the heights of the Snoek peaks are of the same order of magnitude as the background damping. Furthermore, because of the low solid solubility, the alloys studied are super-saturated and the interstitial solute is precipitating from free solution during internal friction measurements. The precipitation of the solute affects the peak temperature and height in an irregular manner rendering the information deduceable from the peaks less self-consistent and less accurate.

2.2 THE HYDROGEN SNOEK PEAK. — It appears that the first evidence of the existence of a hydrogen Snoek peak at about 100 °K (3.7 Hz) in iron has been reported by Chang and Gensamer in 1953 [81]. Subsequent studies [82-85] confirmed the existence of the hydrogen Snoek peak in the temperature range from 30° to 50 °K at 1 Hz. However, the information was still insufficient to make quantitative deductions concerning the behaviour of hydrogen in iron. More recently, Gibala [86] has re-examined the peak in greater detail and has confirmed that the peak is a Snoek relaxation peak due to hydrogen and that it occurs at 31 °K (1 Hz). The associated activation energy and the attempt frequency of the relaxation process have been determined to be 2 kcal.mol⁻¹ and 6 x 10¹³ s⁻¹ respectively.

Heller [84] outgassed the hydrogen charged specimen to remove hydrogen and then charged it with deuterium. On subsequent internal friction measurements he observed a peak at a slightly higher temperature with the associated activation energy also higher (by 700 cal.mol⁻¹) than that for hydrogen (3 000 cal.mol⁻¹). This peak was suggested to be caused by stress-induced ordering of deuterium.

The hydrogen Snoek peak was also observed and identified in tantalum [87, 88] and in niobium [87, 89]. As in the case of iron a peak at a higher temperature was observed in hydrogen outgassed and deuterium charged niobium [89]. The thermodynamic parameters of the hydrogen and deuterium peaks in niobium, tantalum and iron are given in Table II. The activation energies associated with the stress-induced ordering of the hydrogen atom are of the same order of magnitude as that for the diffusion of hydrogen in iron [86], niobium [90] and tantalum [91].

<table>
<thead>
<tr>
<th>System</th>
<th>Peak Temp. (°K)</th>
<th>Applied Freq. (Hz)</th>
<th>Activ. Energy (cal.mol⁻¹)</th>
<th>Attempt Freq. (s⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-H</td>
<td>~ 100</td>
<td>3.7</td>
<td>—</td>
<td>—</td>
<td>Chang, Gensamer [81]</td>
</tr>
<tr>
<td>Fe-H</td>
<td>50</td>
<td>20</td>
<td>~ 3000</td>
<td>—</td>
<td>Weiner, Gensamer [82]</td>
</tr>
<tr>
<td>Fe-H</td>
<td>30</td>
<td>1.4</td>
<td>~ 3000</td>
<td>—</td>
<td>Heller [83]</td>
</tr>
<tr>
<td>Fe-D</td>
<td>35</td>
<td>1.4</td>
<td>3700</td>
<td>—</td>
<td>Heller [83]</td>
</tr>
<tr>
<td>Fe-H</td>
<td>50</td>
<td>35000</td>
<td>—</td>
<td>—</td>
<td>Hewitt [85]</td>
</tr>
<tr>
<td>Fe-3.5Ni-H</td>
<td>35</td>
<td>35000</td>
<td>—</td>
<td>—</td>
<td>Hewitt [85]</td>
</tr>
<tr>
<td>Fe-H</td>
<td>48</td>
<td>80000</td>
<td>2000</td>
<td>6 x 10¹³</td>
<td>Gibala [86]</td>
</tr>
<tr>
<td>Nb-H</td>
<td>100</td>
<td>30700</td>
<td>4200</td>
<td>3.5 x 10¹³</td>
<td>Cannelli, Verdini [87]</td>
</tr>
<tr>
<td>Nb-H</td>
<td>77</td>
<td>400</td>
<td>2800</td>
<td>1.9 x 10¹⁰</td>
<td>Schiller, Schneiders [89]</td>
</tr>
<tr>
<td>Nb-D</td>
<td>105</td>
<td>400</td>
<td>4200</td>
<td>1.3 x 10¹¹</td>
<td>Schiller, Schneiders [89]</td>
</tr>
<tr>
<td>Ta-H</td>
<td>90</td>
<td>20000</td>
<td>2800</td>
<td>1.0 x 10¹¹</td>
<td>Cannelli, Verdini [88]</td>
</tr>
<tr>
<td>Ta-D</td>
<td>126</td>
<td>20000</td>
<td>2800</td>
<td>1.2 x 10⁹</td>
<td>Cannelli, Verdini [88]</td>
</tr>
</tbody>
</table>

2.3 ACTIVATION ENERGY OF THE STRESS-INDUCED ORDERING. — The Snoek relaxation process involves stress-induced migration of interstitial atoms in the BCC lattice and therefore the relaxation time (τ) is governed by the diffusion coefficient (D) of the migrating atom. In fact for BCC lattices [6, 7]

$$\tau = \frac{a^2}{36D}$$  \hspace{1cm} (1)

where $a$ is the lattice parameter and $D$ is given by

$$D = D_0 \exp(-H/RT)$$  \hspace{1cm} (2)

where $H$ is the activation energy for diffusion of the interstitial atom. Within experimental errors of the different methods used for the determination of $H$ and $Q$, the activation energy for the stress-induced ordering, the agreement between $H$ and $Q$ is good [6, 7].

Wert and Marx [79] pointed out that the activation energy ($Q$) for the Snoek relaxation process divided by the corresponding peak temperature ($T$°K) is a constant. By plotting the available data at that time they obtained a linear relationship between $Q$ and $T$ with the straight line going through the
origin. This relationship was justified theoretically by the equation

\[ Q = T \ln (v/f) + 2S \]  

(3)

where \( v \) is the atomic frequency and \( S \) is the activation entropy. Equation (3) was derived by Marx and Wert from the theory of interstitial atomic diffusion coefficients [92]. More recently, Stephenson [93] re-examined the relationship of equation (3) with additional and more accurate internal friction data on the diffusion of interstitial solute atoms in BCC metals. He confirmed the validity of the relationship and from the analysed data reported that

\[ Q = 62.1 T \pm 890 \text{cal.mol}^{-1}. \]  

(4)

The relationship derived by Wert and Marx is useful in the identification of Snoek relaxation peaks in internal friction spectra where the peaks are not completely self-evident, i.e., in the iron-hydrogen system. It is seen from Table III that there are appreciable discrepancies between the values of \( K \) for the same alloy system. Besides the orientation factor [22] already discussed (Section 2) \( K \) depends on the uncertainty arising from the experimental limitations of the chemical analyses and the limits in the determination of the peak height. Other factors affecting \( K \) are grain and subgrain boundaries, substitutional solutes (Section 2.7.1), thermal and mechanical treatments, dislocations, and other defects that tend to remove the interstitial atom from free solution. Some of these factors have been reviewed by Leak [71] in 1960.

In iron the variation of \( K \) with grain size was studied by a number of workers [67, 69, 72-74, 94-98] who showed that \( K \) decreased with increasing grain size in the manner illustrated in figure 1. The explanations put forward to account for the variation of \( K \) with grain size are: (a) The interstitial atoms near grain boundaries are immobilized by the stress fields of the boundaries and do not take part in the stress-

Table III

<table>
<thead>
<tr>
<th>System</th>
<th>Average ( K )</th>
<th>Peak Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-O</td>
<td>1.30</td>
<td>—</td>
<td>34</td>
</tr>
<tr>
<td>Nb-O</td>
<td>1.16</td>
<td>139</td>
<td>32</td>
</tr>
<tr>
<td>Nb-O</td>
<td>1.25</td>
<td>155</td>
<td>58</td>
</tr>
<tr>
<td>Nb-O</td>
<td>1.30</td>
<td>~150</td>
<td>36</td>
</tr>
<tr>
<td>Nb-O</td>
<td>0.845</td>
<td>156</td>
<td>59</td>
</tr>
<tr>
<td>Nb-N</td>
<td>0.93</td>
<td>—</td>
<td>34</td>
</tr>
<tr>
<td>Nb-N</td>
<td>0.95</td>
<td>275</td>
<td>35</td>
</tr>
<tr>
<td>Nb-N</td>
<td>1.35</td>
<td>270</td>
<td>60</td>
</tr>
<tr>
<td>Nb-N</td>
<td>1.04</td>
<td>288</td>
<td>61</td>
</tr>
<tr>
<td>Ta-O</td>
<td>0.29</td>
<td>142</td>
<td>30</td>
</tr>
<tr>
<td>Ta-O</td>
<td>0.24</td>
<td>~195</td>
<td>62</td>
</tr>
<tr>
<td>Ta-O</td>
<td>0.48</td>
<td>155</td>
<td>33</td>
</tr>
<tr>
<td>Ta-O</td>
<td>0.31</td>
<td>~195</td>
<td>63</td>
</tr>
<tr>
<td>Ta-N</td>
<td>0.38</td>
<td>170</td>
<td>64</td>
</tr>
<tr>
<td>Ta-N</td>
<td>0.23</td>
<td>329</td>
<td>31</td>
</tr>
<tr>
<td>Ta-N</td>
<td>0.37</td>
<td>~380</td>
<td>63</td>
</tr>
<tr>
<td>Ta-C</td>
<td>0.13</td>
<td>338</td>
<td>31</td>
</tr>
<tr>
<td>V-O</td>
<td>0.16</td>
<td>180</td>
<td>32</td>
</tr>
<tr>
<td>V-O</td>
<td>0.35</td>
<td>186</td>
<td>42</td>
</tr>
<tr>
<td>V-N</td>
<td>0.26</td>
<td>278</td>
<td>43</td>
</tr>
</tbody>
</table>

Section 2.2) and Group VIA metal — interstitial solute atom systems (Section 2.1.2).

2.4 RELAXATION STRENGTH OF THE SNOEK PEAK. — The relaxation strength (\( \delta \)) of the Snoek relaxation peak, as defined by equation (1) is equal to \( 2 \delta_{\text{max}}/\pi \) at the maximum of the peak (\( \delta_{\text{max}} \) when \( \omega r = 1 \). Snoek [21] also showed that \( \delta_{\text{max}} \) in alpha-iron containing either carbon or nitrogen interstitially was proportional to the concentration (C) of the interstitial solute present in free solution, viz.

\[ C = K\delta_{\text{max}} \]  

(5)

where \( K \) is the proportionality constant frequently referred to as the « conversion factor ». In 1947 Dijkstra [22] confirmed the validity of equation (5). Since then many experimental verifications of the relationship of equation (5) have been reported for various BCC metals and the available values of \( K \) are given in Table III.

It is seen from Table III that there are appreciable discrepancies between the values of \( K \) for the same alloy system. Besides the orientation factor [22] already discussed (Section 2) \( K \) depends on the uncertainty arising from the experimental limitations of the chemical analyses and the limits in the determination of the peak height. Other factors affecting \( K \) are grain and subgrain boundaries, substitutional solutes (Section 2.7.1), thermal and mechanical treatments, dislocations, and other defects that tend to remove the interstitial atom from free solution. Some of these factors have been reviewed by Leak [71] in 1960.
induced ordering [69]. (b) An appreciable fraction of interstitial solute diffuses to the boundaries during quenching from the solution treatment or recrystallisation temperature [97, 99]. Thus for a given interstitial solute content, the fraction remaining in free solution decreases with decreasing grain size (increasing grain boundary area), resulting in lower Snoek peak and hence higher value of \( K \). (c) Since for single crystals \( K \) is minimum (peak height maximum), when the stress is applied in the \(< 100 >\) direction, and infinitely large (peak height essentially zero), when the stress is applied in the \(< 111 >\) direction, \( K \) varies between these two extreme values when the stress is applied in directions between \(< 100 >\) and \(< 111 >\) [22-24, 98].

For relative comparison of relaxation strengths (A) of various systems one should use \( A \) (eq. (1)) per atomic per cent interstitial solute i.e. \( A = 2/(\pi K) \) where \( K \) (eq. (5)) is in units of atomic per cent. From Polder’s theory [100] \( A = A(T - aT_c) \) where \( A \) and \( a \) are constant, and \( T_c \) a critical ordering temperature (ºK). Consequently Powers and Doyle [32] compiled \( A \) for a number of systems at temperatures of the Snoek peak and 0.1 \( T_M \), where \( T_M \) (ºK) is the melting point of the pure solvent metal. The values range from 0.1 to 0.6 and from 0.13 to 1.25 for the first and second case respectively. Subsequently Berry and Nowick [5] and Beshers [101] re-examined the values of \( A \) compiled by Powers and Doyle, but were unsuccessful to produce a conclusive hypothesis concerning the relaxation strength of the Snoek peak.

2.5 OCTAHEDRAL VERSUS TETRAHEDRAL INTERSTITIAL SITE. — The assumption made by Snoek [21] that dissolved carbon and nitrogen atoms occupy the octahedral interstitial sites of the BCC lattice of iron is consistent with X-ray [102, 103] and other evidence, which indicates that carbon [104] and nitrogen [105] in martensite occupy the octahedral \((\frac{1}{2}, 0, 0)\) sites. It is, however, inconsistent with the view that interstitial solute atoms should occupy the larger interstitial site, which is the tetrahedral interstice, viz. \((\frac{1}{4}, \frac{1}{4}, 0)\) (Fig. 2). Using the criterion of minimum strain energy to decide the position of the interstitial solute atoms, it is found that indeed the octahedral site is occupied. Dijkstra [22] showed that the asymmetry associated with tetrahedral sites, and therefore the relaxation strength per solute atom, would be much less (for iron by a factor of 1 000) than that for the octahedral sites.

Powers and Doyle [32], comparing the relaxation strength per atom per cent interstitial solute for a number of systems, observed that the values showed a spread ranging from one third to two of the values for carbon and nitrogen in iron. Consequently, they concluded that it was reasonable to assume that the interstitial atoms in these systems occupy the octahedral sites as in iron.

Berry and Nowick [5] re-examined the relaxation strengths compiled by Powers and Doyle confirmed Dijkstra’s premise and found no reason to doubt the octahedral occupancy in systems other than iron-carbon and iron-nitrogen.

Beshers [101] carried out a detailed study of interstitial sites in the BCC lattice, and questioned the validity of Dijkstra’s premise. Discussing the distortions caused by interstitial solutes and the associated elastic strain energies, he derived the expression

\[
R = \frac{A'}{(QE_{100})}
\]

where \( A' \) is the relaxation strength obtained experimentally and referred to a common temperature, \( Q \) the activation energy for stress-induced migration, and \( E_{100} \) the Young’s modulus. Beshers uses \( R \) as a criterion to determine whether the octahedral or tetrahedral site should be preferred. High values of \( R \) should indicate the preference for octahedral site occupation, low values for tetrahedral site occupation.
According to this criterion carbon and nitrogen in alpha-iron, carbon in tantalum and oxygen in vanadium should occupy the octahedral sites, whereas oxygen and nitrogen in tantalum and niobium, and nitrogen and carbon in vanadium should occupy the tetrahedral sites.

### 2.6 The Snoek Peak in Other-than-BCC Metals.

**2.6.1 The FCC Metals.** — The symmetry of the interstitial sites in FCC lattices is such that interstitial solute atoms do not introduce a directional distortion, as is the case in BCC lattices. This is also true for substitutional solute atoms. Consequently, stress-induced ordering of isolated point defects, hence the Snoek peak, is not expected in FCC lattices. The internal friction peaks due to diffusion of interstitial solute atoms in FCC lattices, that have been reported are normally accounted for in terms of atoms associated as pairs (sections 2.7.2 and 4.2).

2.6.2 The HCP Metals. — There have been a number of investigations attempting to show that interstitial solute atoms in HCP crystals exhibit mechanical relaxation. In Table IV are given the observed peaks in z-zirconium and x-titanium containing hydrogen. Some of the authors attributed the peak to the stress-induced ordering of hydrogen atoms passing from octahedral to tetrahedral sites [106, 108]. Others explained their peaks as being due to stress-induced redistribution of hydrogen atoms occupying tetrahedral sites [107, 109]. A disagreement, therefore, exists as to which of the mechanisms is actually operative.

### Table IV

<table>
<thead>
<tr>
<th>System</th>
<th>Peak Temperature (°C)</th>
<th>Applied Frequency (Hz)</th>
<th>Activation Energy (kcal mol⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>αZr-H</td>
<td>-45</td>
<td>1.4</td>
<td>11.6</td>
<td>Bungardt, Preisendanz [107]</td>
</tr>
<tr>
<td>αZr-H</td>
<td>160</td>
<td>∼ 500</td>
<td>~ 11.6</td>
<td>Haziguti et al. [108]</td>
</tr>
<tr>
<td>αZr-H</td>
<td>-129</td>
<td>1.6</td>
<td>4.6</td>
<td>Povolo, Bisogni [110]</td>
</tr>
<tr>
<td>αZr-H</td>
<td>-43</td>
<td>1.6</td>
<td>12.0</td>
<td>Povolo, Bisogni [110]</td>
</tr>
<tr>
<td>αTi-H</td>
<td>0</td>
<td>3.4</td>
<td>15.0</td>
<td>Küster et al. [107]</td>
</tr>
</tbody>
</table>

Theoretical attempts have also been made to solve this problem and in this case the situation is controversial too. Bovarnik [111] using geometrical considerations, and Povolo and Bisogni [19], using the group theory method [16-18] conclude that it is not possible to have stress-induced ordering of solute atoms in HCP structures. Beshers [101], and Nowick and Heller [18], on the other hand, propose that under certain conditions it would be possible to have mechanical relaxation due to interstitial atoms occupying either octahedral or tetrahedral sites in HCP structures. Povolo and Bisogni have also shown that an internal friction peak due to isolated point defects in HCP crystals can only be produced by stress-induced ordering of the defects between octahedral-tetrahedral sites [19].

In view of the above it would appear that the observed peaks in z-zirconium and x-titanium are due to stress-induced ordering of hydrogen between octahedral and tetrahedral sites. More recently, however, Povolo and Bisogni [110] have carried out a detailed study of the zirconium-hydrogen system over the temperature range from -200° to 120°C and have reported three peaks. Neither of these peaks has been accounted for in terms of the stress-induced ordering of hydrogen between octahedral-tetrahedral sites. These peaks were actually interpreted as being due to an interaction between dislocations and hydrogen atoms in the α-phase and the stress-induced migration of hydrogen atoms within the γ-hydride respectively. The mechanism of stress-induced ordering of hydrogen atoms between octahedral-tetrahedral sites has only been used as an alternative model to interpret the peaks occurring at -129° and -43°C. Thus the possibility of stress-induced ordering of isolated point defects in the HCP metals remains unresolved.

2.6.3 Miscellaneous Lattices. — Southgate [112-114] has reported internal friction peaks in silicon and germanium (diamond structures) containing interstitial oxygen. In silicon the peak occurs at 1 030°C and in germanium at 770°C at a frequency of 100 kHz. The associated activation energies of the relaxation processes as obtained by Haas [115], from the data of Southgate, are 58.5 kcal mol⁻¹ and 46.5 kcal mol⁻¹ for silicon and germanium respectively.

The position and the path of the stress-induced motion of the oxygen atom in the diamond structure is shown in figure 3. The oxygen atom forms a non-linear Si-O-Si configuration with the nearest neighbour silicon atoms [116]. The stress-induced motion resulting in the relaxation peak is motion <<a>> which involves long-range diffusion as compared with the rotating motion <<b>>.

Recently an internal friction peak has been reported [117-119] in uranium oxide (a fluorite structure) containing interstitial oxygen. At a frequency of 53 MHz the peak occurs at 105°C. The relaxation mechanism causing the peak has been interpreted as the stress-induced ordering of interstitial [120].
oxygen atoms in UO$_3$ [118]. The associated activation energy and the attempt frequency of the relaxation process have been determined as 11.2 kcal mol$^{-1}$ and $1.5 \times 10^{13}$ s$^{-1}$ respectively.

2.7 INTERSTITIAL SOLUTE INTERACTION PEAKS. —

2.7.1 The BCC Metals. — The first Snoek peaks observed by Ké [25, 26] in BCC metals other than alpha-iron were those due to oxygen and nitrogen in tantalum. The unusual feature of these peaks was their breadth which, at half-width, was 50 to 70 % greater than that expected from a single relaxation process. Subsequently the broadening effect was confirmed in tantalum containing varying amounts of oxygen and nitrogen, and attributed to the tendency of interstitial atoms to form clusters. In figure 4 is illustrated the variation of the width of the nitrogen Snoek peak in tantalum with increasing nitrogen content [30].

More detailed studies of the multiple relaxations have since been carried out by a number of workers [32, 121-123, 38]. Powers and Doyle [32] have shown that the broadened Snoek peak due to oxygen in tantalum could be adequately described by two relaxation processes, one involving single oxygen atoms and the other associated pairs of oxygen atoms. In iron-carbon and iron-nitrogen alloys Keefer and Wert [121, 122] found similar evidence for interstitial clustering. They identified four relaxation processes three out of which they interpreted as being due to stress-induced ordering of nitrogen atoms as singles, pairs and triplets [122]. In alloys of oxygen in niobium Gibala and Wert [123] identified four relaxation peaks due to singles, pairs, triplets and quadruplets of oxygen atoms. Recently Ahmad and Szkopiak [38] carried out a detailed study of the broadening effect of the Snoek peak in niobium-oxygen and niobium-nitrogen alloys. They observed three peaks for each alloy due to singles, pairs and triplets of the respective interstitial solute atom.

Ahmad and Szkopiak did not observe the quadruplet peak, even in the presence of precipitates of nitrides in the niobium-nitrogen alloy. They therefore concluded that clusters containing more than three atoms do not cause relaxation.

Besides the relaxations caused by pairs of like interstitial atoms there is evidence of stress-induced ordering due to pairs of unlike interstitial atoms in tantalum [30] and niobium [36, 124, 38] containing both oxygen and nitrogen. This peak occurs at a temperature slightly higher than that at which the oxygen triplets peak occurs. The peak, which Gibala and Wert [123] interpreted as being due to quadruplets of oxygen atoms in niobium, can, therefore, be equally well interpreted [38] as an oxygen-nitrogen interaction peak [36, 124].

The attractive interactions of interstitial atoms to form pairs and triplets can be described by elastic theory [125]. Unfortunately, each of the clusters may assume more than one possible configuration in the lattice [126], and it is not known which of these represents the stable configuration. There is, however, indication that the atoms in pairs and triplets are not nearest neighbours [126], and that the stress-induced ordering associated with pairs and triplets involves only one atom jumping under the influence of the companion atoms which remain stationary [38]. Since the atoms taking part in the relaxation process jump within the stress fields of their companion atoms, the associated activation energy of the process is greater than that for singles, and increases with the size of the cluster (Table V). The increase in the energy...
appears to be of the order of magnitude of the binding energy of the cluster [122]. The results of Table V are self-consistent, with the exception of the tantalum-oxygen system, and indicate that the binding energies of pairs and triplets are about 1.5 to 2.0 and 3 to 4 kcal mol⁻¹ respectively, irrespective of the alloy system.

### TABLE V

**Activation energies for stress-induced ordering of singles, pairs and triplets of interstitial solute atoms in BCC metals.**

<table>
<thead>
<tr>
<th>System</th>
<th>Singles</th>
<th>Pairs</th>
<th>Triplets</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-O</td>
<td>25500</td>
<td>32000</td>
<td>21000</td>
<td>Powell [29]</td>
</tr>
<tr>
<td>Fe-N</td>
<td>17500</td>
<td>19000</td>
<td>21000</td>
<td>Keefe, Wert [122]</td>
</tr>
<tr>
<td>Nb-O</td>
<td>26800</td>
<td>28000</td>
<td>29300</td>
<td>Gibala, Wert [123]</td>
</tr>
<tr>
<td>Nb-O</td>
<td>26500</td>
<td>28000</td>
<td>29500</td>
<td>Ahmad, Szkopiak [38]</td>
</tr>
<tr>
<td>Nb-N</td>
<td>34900</td>
<td>36500</td>
<td>37000</td>
<td>Ahmad, Szkopiak [38]</td>
</tr>
</tbody>
</table>

### 2.7.2 The FCC Metals.

Internal friction peaks due to stress-induced ordering of pairs of interstitial atoms in FCC metals are also known. There is a number of reports showing the existence of relaxation peaks due to pairs of carbon atoms in nickel [127-130] and cobalt [131], hydrogen and deuterium in palladium [132], and oxygen in silver [133]. The main characteristics of these peaks are that (a) the peak heights are comparatively low, (b) the widths of the peaks are up to 25% wider than that for single relaxation time, and (c) the associated activation energy of the relaxation process is in good agreement with that for the diffusion of the interstitial atom. The thermodynamic parameters of some of these peaks are given in Table VI.

Similar peaks due to carbon pairs have also been reported [134, 135] in gamma-iron containing different substitutional alloying elements. Recently, however, it has been pointed out [136] that these peaks are more likely to be due to stress-induced ordering of single carbon atoms jumping in the vicinity of substitutional solute atoms (Section 4.2). The existence of relaxation peaks due to carbon pairs in such alloys is not precluded, but the peaks are probably not evident in the presence of the stronger relaxation resulting from the interstitial-substitutional pair.

3. The Zener relaxation peak. — In 1943 Zener [137] reported an internal friction peak at 420°C (600 Hz) in alpha-brass single-crystal. This alloy is a FCC substitutional solid solution. Since that time, the existence of relaxation peaks having similar characteristics, have been confirmed in numerous solid solutions. Most examples are found in FCC alloys, and include copper-zinc [138], silver-zinc [139], gold-nickel [140], aluminium-copper [141], copper-gold [142]. These peaks have also been documented in BCC alloys, namely iron-vanadium [143], iron-aluminium [144], lithium-magnesium [145] and iron-chromium [146], and HCP solid solution, e.g. magnesium-cadmium [147].

The characteristic features of the Zener relaxation peaks are:

- a) The peaks are a general property of substitutional solid solutions.
- b) The relaxation strength is strongly dependent on the concentration (C) of the alloy. For lower concentrations the peak height is approximately proportional to C² [148], whilst at higher concentrations to C² (1 - C²) [149].
- c) The relaxation strength (Δ) is temperature dependent [150], viz.
  \[ Δ = T_0 / (T - T_c) \]
  where T₀ is a constant and T_c is the critical temperature for spontaneous ordering.
- d) The relaxation strength decreases as the state of long range order increases [147, 149, 151] and would be zero in perfectly ordered alloys.
- e) The relaxation strength measured in single crystals shows marked anisotropy. It is about an order of magnitude greater when the stress is applied in the <100> direction as compared with the <111> direction [141, 148].
- f) The associated activation energy of the Zener relaxation process, in general, is about 10% lower than that for diffusion determined by chemical or
ANELASTIC EFFECTS DUE TO POINT DEFECTS IN SOLIDS

This difference is mainly due to the fact that techniques based on bulk diffusion measure the average atomic jump rate over different types of atomic sites [6, 152]. Internal friction measurements, on the other hand, are related specifically to the ordering of atoms associated in pairs or clusters of higher order.

g) The observed peaks are up to about 20% broader than a Debye peak. The best explanation of the broadening effect appears to be the log-normal distribution in the relaxation time of the process [153, 154].

The Zener relaxation process undoubtedly arises from the stress-induced ordering of solute atoms in substitutional solid solutions. The first theory that has been presented to account for the relaxation process is the "pair re-orientation theory" put forward by Zener himself [155]. According to this theory the relaxation is caused by re-orientation of pairs of nearest-neighbour solute atoms into preferred orientations under the influence of applied stresses.

The pair concept is reasonably valid for low concentrations of solute (up to about 10%), but breaks down at higher concentrations (20-50%) because of the presence of aggregates containing more than two atoms [156]. LeClair and Lomer [149] developed a more general theory known as "directional ordering theory" based on a model in which the atomic configuration is expressed by directional order parameters defined in terms of the pair-wise grouping. In this case relaxation is caused by reversible directional-short-range order in a stressed crystal.

The greatest weakness of the theories of the Zener relaxation is the fact that they are based on nearest-neighbour configurations. Seraphin and Nowick [148] have pointed out that the active element of the Zener relaxation process is the solute-solute pair in the next-nearest-neighbour, rather than the nearest-neighbour configuration. More recently Haven [157] has suggested that in considering the Zener relaxation process in disordered FCC solid solutions, besides the reorientation of pairs, the dissociation of pairs should also be considered. It, therefore, appears that the mechanism of the Zener relaxation process is visualised as a more general case of stress-induced ordering than the rigid pair orientation model originally suggested.

The Zener relaxation peak has also been reported in ternary solid solutions of gold-silver-zinc [158] and copper-nickel-zinc [159]. The peaks in these alloys have, in most respects, the same characteristics as those in binary alloys. One difference, that should be singled out, is the fact that the half-width of the peak is much greater in ternaries than that in binaries. The broadening effect, as pointed out by Coleman and Wert [159], is due to the superimposition of relaxation processes with different activation energies. These relaxations most likely arise from various interactions between the solvent and the two solute atoms [159]. The Zener peak can, therefore, be used to study diffusion and possibly association of atoms in ternary solid solutions in the same way as in binaries.

It should be noted that there is some evidence of the existence of Zener peaks in quaternary alloys [160]. In these alloys, however, the peaks are difficult to study, because of their transient nature.

4. Interstitial substitutional solute interaction peaks.

 — Internal friction peaks due to stress-induced ordering of interacting combinations of elementary point defects so far discussed involved like or unlike atoms of the same type. In this section relaxations are reviewed which involve stress-induced ordering of interacting combinations of interstitial-substitutional atoms.

4.1 The BCC Metals. — The most extensively studied ternary alloys containing interstitial and substitutional solute atoms are those based on iron [161-172] in particular iron-manganese-nitrogen alloys [167-172]. In the presence of manganese the normal Snoek peak (Section 2) due to stress-induced ordering of interstitial nitrogen atoms in the BCC lattice of iron becomes broadened and distorted (Fig. 5). The distorting effect depends on the substitutional solute atom and its concentration, and is due to the superimposition of additional peaks on the normal Snoek peak. In Table VII are given peak

![Fig. 5. — Comparison of an internal friction curve for an iron-manganese-nitrogen ternary alloy with theoretical curve for iron-nitrogen binary alloy.](image-url)
TABLE VII

Temperatures of the additional peak in iron-nitrogen containing different substitutional solutes (after Lagerberg [163])

<table>
<thead>
<tr>
<th>Solute</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>32</td>
</tr>
<tr>
<td>Chromium</td>
<td>45</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>75</td>
</tr>
<tr>
<td>Vanadium</td>
<td>87</td>
</tr>
<tr>
<td>Normal Snoek peak</td>
<td>22</td>
</tr>
</tbody>
</table>

Temperatures of the additional peak in alloys of iron-nitrogen containing 0.5 wt.% of different substitutional solute atoms [163]. The addition of nickel to iron, however, does not introduce any additional peaks [171]. Additional peaks in iron-carbon alloys containing substitutional solute atoms [173] have also not been reported so far.

The relaxation mechanism causing the additional peak in the ternary alloys has been interpreted as being the stress-induced migration of nitrogen atoms from an octahedral site having an iron and a substitutional manganese atom as nearest neighbours [161] (site N in Fig. 6). In this configuration the nitrogen atom has two jumping modes under stress. One is to an equivalent iron-manganese site [162, 164, 165, 171] and the other is to the normal iron-iron octahedral site [161, 164, 165, 167, 170]. It has also been suggested that relaxation can occur due to the nitrogen atoms jumping from iron-iron to iron-manganese octahedral sites under the influence of stress [162, 164, 165]. Another modification of the octahedral site in the ternary alloys is the replacement of the nearest neighbours of the site by a pair of substitutional solute atoms [168].

Gladman and Pickering [168] showed that there are three possible modes for the interstitial solute atom to jump from the next-neighbour pair configuration. In figure 7 is illustrated one-eighth of a unit BCC cell showing a nearest-neighbour pair of manganese atoms and octahedral interstitial sites (crosses) associated with the pair. The dotted lines indicate connecting paths between these sites which are a/2 and a/√2 away from the nearest and next-nearest manganese atoms respectively. The activation energy of the stress-induced ordering of the nitrogen atom between similar manganese pair sites is expected to be different from the normal iron-iron sites because of the lattice distortion by the manganese atoms. Furthermore, the activation energy may vary according to the path and distance between the two similar octahedral sites, resulting in a broader peak than that normally associated with a single relaxation time. As shown in figure 7 there are three types of jump having lengths a/2, a/√2 and a/√3/2.

![Fig. 6. Octahedral sites in the vicinity of a manganese atom in the BCC iron crystal. The sites marked N are nearest-neighbor and that marked X is a next-nearest neighbor.](

![Fig. 7. Model for the interaction between nitrogen and manganese solute atoms in iron.](

The above discussion of the various ways in which nitrogen atoms can cause relaxations indicates that internal friction spectra of the ternary alloys should consist of more than one additional peak. Most of the reports referred to in this section indicated the presence of additional peaks besides the normal Snoek and the main additional peak. In Table VIII are presented parameters characterising such peaks [167, 169-172]. For comparison peaks for an iron-chromium-nitrogen alloy have been included. The peaks 4 and 6 are the normal Snoek and the main additional peak. Most investigators agree that the peak 5 is associated with nitrogen atoms jumping from iron-manganese octahedral sites. There is, however, some uncertainty whether...
the stress-induced jump is made into an equivalent iron-manganese site or the iron-iron site. This problem appears difficult to resolve experimentally. The peak 7 is believed to be associated with carbon pairs [171, 172]. The remaining three peaks, 1, 2 and 3 have been suggested to be associated with nitrogen atoms jumping in the vicinity of a pair of manganese atoms [168, 171, 172]. It is, however, difficult to distinguish between the three possible modes of jumping suggested by Gladman and Pickering [168]. Couper and Kennedy [170] who reported only one peak occurring at a temperature between those of peaks 2 and 3 (Table VIII), suggested that the peak consists of two peaks: one due to stress-induced ordering of nitrogen atoms associated with pairs of manganese atoms (in agreement with refs 168, 171 and 172) and the other due to nitrogen atoms jumping from iron-iron octahedral sites into iron-manganese sites.

### Table VIII

<table>
<thead>
<tr>
<th>Manganese Content (wt. %)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>Peak 6</th>
<th>Peak 7</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (°C)</td>
<td>$Q$ (cal. mol$^{-1}$)</td>
<td>$T$ (°C)</td>
<td>$Q$ (cal. mol$^{-1}$)</td>
<td>$T$ (°C)</td>
<td>$Q$ (cal. mol$^{-1}$)</td>
<td>$T$ (°C)</td>
<td>$Q$ (cal. mol$^{-1}$)</td>
</tr>
<tr>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>15000</td>
<td>24</td>
<td>18000</td>
<td>35</td>
<td>21100</td>
</tr>
<tr>
<td>0.2-1.6</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>14000</td>
<td>26</td>
<td>16200</td>
<td>36</td>
<td>17000</td>
</tr>
<tr>
<td>0.1-1.6</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>16500</td>
<td>23</td>
<td>18500</td>
<td>34.5</td>
<td>19500</td>
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<tr>
<td>0.9</td>
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<td>15800</td>
<td>3</td>
<td>16700</td>
<td>10</td>
<td>17500</td>
<td>23</td>
<td>18600</td>
</tr>
<tr>
<td>0.3-1.4</td>
<td>-8.5</td>
<td>15800</td>
<td>3.5</td>
<td>16700</td>
<td>10</td>
<td>17500</td>
<td>24</td>
<td>18600</td>
</tr>
<tr>
<td>0.94 Cr</td>
<td>-6</td>
<td>16200</td>
<td>6.0</td>
<td>17000</td>
<td>-</td>
<td>-</td>
<td>24</td>
<td>18600</td>
</tr>
<tr>
<td>Enrietto [167]</td>
<td>Nacken, Kublmann [169]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Couper, Kennedy [170]</td>
<td>Ritchie, Rawlings [171]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ritchie, Rawlings [171]</td>
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<tr>
<td>Ritchie, Rawlings [171]</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

In iron-vanadium-nitrogen alloys the additional peak is more complex as originally believed [161], because of the high affinity of vanadium for nitrogen. The peak was broader than in iron-manganese-nitrogen alloys, and after prolonged soaking at 950 °C it became narrower and occurred at a higher temperature (88 °C) than in quenched specimens (80 °C). At first it was suggested that the peak was due to stress-induced ordering of nitrogen atoms occupying octahedral sites around fine precipitates of vanadium nitride [174]. Subsequently it was explained in terms of nitrogen atoms jumping from the iron-vanadium octahedral sites [175]. Jamieson and Kennedy [176] on the other hand, ascribed the appearance and behaviour of the peak to both mechanisms. Perry et al. [177] who separated the peak into three constituent peaks, proposed the existence of three modes of relaxation of nitrogen atoms occupying octahedral sites associated with the vanadium atom. Recently, Szabo-Miszenti [178] studied iron-titanium-nitrogen alloys and reported two peaks occurring in the temperature ranges 116-166 °C and 221-242 °C (1 Hz). These peaks have been tentatively considered to be due to relaxations of nitrogen atoms associated with titanium solute atoms.

Summarising the interaction peaks observed in internal friction spectra of iron-substitutional-interstitial ternary alloys the following general observations can be made.

a) The occurrence of the peaks depends on the chemical affinity of the substitutional solute atom for the interstitial solute atom.

b) The interaction peaks occurring at temperatures higher than that of the normal Snoek peak of the interstitial solute are due to stress-induced ordering of the interstitial atom occupying iron-substitutional solute octahedral sites.

c) The interaction peaks occurring at temperatures lower than that of the normal Snoek peak are due to stress-induced ordering of the interstitial atom being associated with nearest-neighbour pairs of the substitutional solute atoms. These peaks frequently consist of up to three separate peaks, each caused by a relaxation process with a different associated activation energy.

Interstitial-substitutional solute atom interaction peaks have also been reported for dilute niobium-zirconium-oxygen [179-182] niobium-zirconium-nitrogen [32, 179-181, 183] and niobium-iron-nitrogen ternary alloys [181]. In the case of the niobium-zirconium alloys, additional peaks due to stress-induced ordering of both oxygen and nitrogen atoms associated with the substitutional zirconium solute atoms have been observed. In niobium-iron alloys, on the other hand, additional peaks due to interstitial solute atoms associated with the iron atoms were observed for oxygen only. No such peaks were observed for oxygen, although the normal Snoek peak due to
oxygen was reduced by the presence of iron in solid solution [181]. It, therefore, appears that, as in the case of iron, chemical affinity of the substitutional solute atoms for the interstitial atoms is playing an important role in the complex relaxations in niobium.

The additional peaks in niobium-substitutional-interstitial ternary alloys are also accounted for in terms of associations of interstitial solute atoms with singles [182, 183] and pairs [183] of substitutional solute atoms. Furthermore Miner et al. [182] suggest that a peak caused by stress-induced ordering of an interstitial atom associated with a pair of substitutional atoms can be equally well interpreted in terms of a pair of interstitial atoms occupying nearest-neighbour octahedral sites to a single substitutional solute atom.

4.2 The FCC Metals. — In Section 2.6.1 it has been stated that pure FCC crystals do not exhibit anelastic relaxation. Impure or alloyed FCC crystals, on the other hand, have been reported to show relaxation peaks in their internal friction spectra. Extensive studies by Kê and his co-workers of austenitic steels [184-186] and nickel-iron alloys [187] revealed the existence of internal friction peaks in these materials containing interstitial carbon. More recently Mah and Wert [188] reported relaxation peaks in yttrium containing oxygen or nitrogen as interstitial impurities. These peaks were described as being caused by stress-induced ordering of the interstitial atoms associated with substitutional solute atoms. Peterson et al. [189] attributed the peak at 205 °K (80 kHz), occurring in the internal friction spectrum of hydrogen-charged austenitic stainless steel, to a relaxation process involving a hydrogen-substitutional solute atom pair. Recently, Kandarpa and Spretnak [190] reported a peak in iron-15 to 40 % manganese-carbon ternary alloys. This peak is believed to be caused by stress-induced ordering of carbon atoms associated with manganese atoms.

The model used by Kê and his co-workers to describe the relaxation process causing the observed peak in FCC substitutional solid solutions containing interstitial solute atoms is illustrated in figure 8. The interstitial solute atoms occupy sites (a, b or c) which are nearest-neighbours to the substitutional impurity atom. Under stress the interstitial atom produces an anelastic strain by moving between a-b, or a-c sites. The model was based on the fact that the relaxation strength of the peak varied linearly with interstitial content. Such variation has also been reported in the iron-manganese-carbon alloys [190] lending support to the validity of the model.

4.3 The HCP Metals. — A number of investigations carried out in recent years report the existence of internal friction peaks associated with interstitial solute atoms in HCP metals containing substitutional impurities [191-196]. Pratt et al. [191] reported a peak at 430 °C (1 Hz) in titanium-oxygen alloys containing 0.1 % iron. Subsequently, Gupta and Weinig [194] also studying the titanium-oxygen alloy containing different substitutional impurities, confirmed the existence of the peak at temperatures between 440° and 470 °C (1 Hz) depending on the substitutional impurity present. Bisogni et al. [192, 195] found internal friction peaks due to the presence of oxygen and nitrogen in a hafnium-6 % zirconium alloy. More recently, Elias and Rawlings [196] reported a peak in a beryllium-0.4 % iron alloy containing interstitial oxygen.

It is apparent from the studies so far carried out that relaxations due to interstitial atoms in HCP metals can only occur in the presence of substitutional solute atoms [194-196]. Furthermore, the relaxation strength of the peak increases with increasing size factor of the substitutional solute atom [194]. The peak has, therefore, been explained as being due to stress-induced ordering of interstitial atoms occupying nearest-neighbour octahedral sites to the substitutional atom [194] (Fig. 9). Recently, Povolo and Bisogni [197] attempted to prove theoretically, using the group theory method [16-18], that the nearest neighbour configuration shown in figure 9 could cause relaxation in HCP metals, confirming the validity of the above model.

5. Relaxation Peaks Due to Intrinsic Point Defects. — In cubic crystals single vacancies and self-interstitials create distortions which also have cubic symmetry. No anelastic effects are, therefore, expected from
ANELASTIC EFFECTS DUE TO POINT DEFECTS IN SOLIDS C2-13

HAFNIUM ATOM

SUBSTITUTIONAL IMPURITY ATOM

VACANT OCTAHEDRAL SITE

OXYGEN IN OCTAHEDRAL* SITE

Fig. 9. — Model for relaxation of an interstitial atom associated with a substitutional atom in a HCP crystal.

Fig. 10. — Configuration of the dumb-bell self-interstitial pair in FCC metals and the two types jumps by which it can change its orientation.

anelastic effects by either a rotation of the dumb-bell pair or a migration jump [198]. The rotation jump does not involve net defect migration, as the centre of gravity of the dumb-bell pair remains unchanged. The migration jump, on the other hand, involves defect migration, as shown in figure 10. Seeger and Wagner [202] reported an internal friction peak in plastically deformed single and poly-crystal nickel, and attributed it to the rotation of dumb-bell pairs of interstitial nickel atoms. The peak occurs at about 70°C (1 Hz) with an associated activation energy of 20 kcal.mol⁻¹ and an attempt frequency of about 6.4 × 10¹² s⁻¹.

Dicaclo and Townsend [203] observed a peak at 200 kO (1 Hz) in deuteron-irradiated tungsten, which was present in the internal friction spectrum after post-irradiation annealing only. Consequently, they suggested that the peak was due to the relaxation of a complex consisting of irradiation-induced defects and impurities. With reference to previous studies, which showed that at the temperature of the peak only self-interstitials were expected to be mobile, Dicaclo and Townsend concluded that the intrinsic defects were self-interstitials. The impurity, on the other hand, was difficult to determine, but considering lattice strains it was suggested that interstitial impurities were the more likely candidates. The peak was characterised by an associated activation energy of 9.2 kcal.mol⁻¹ and an attempt frequency of about 3.2 × 10¹³ s⁻¹.

Dautrepppe, Moser and co-workers [204-206] reported up to four peaks over the temperature range from 80° to 200 °K (0.5 Hz) in both neutron- and electron-irradiated single and polycrystalline iron. These peaks were denoted as I₁ (110 °K), I₂ (126°-129 °K), I₁ (142 °K) and I₂ (158 °K). The peak I₁ was associated with the re-orientation of close interstitial pairs which were characteristic of neutron irradiation. The peaks I₁ and I₂ were attributed to relaxations involving either di-interstitials or di-vacancies. The peak I₁, which appears to have been studied in greater detail, was suggested to be due to stress-induced ordering of pairs of self interstitials. These pairs were believed to have different orientation to those causing the peak I₂. The associated activation energy of the relaxation process causing the peak I₂ was given as 5.8 kcal.mol⁻¹.

Stanley and Szkopiak studied the so-called β peak [207] in irradiated [208], cold-worked [209] and quenched [210] commercial niobium. The peak occurred over the temperature range from 180° to 230 °C (1 Hz), and consisted of at least three constituent peaks. The main characteristics of the peak are that:

a) It was absent after deformation at, and quenching to, room temperature. It was, however, present after irradiation, because this treatment was carried out at 60 °C.

b) It appeared after, and was enhanced by, post-treatment annealing.

c) Its overall relaxation strength was highest for the quenched material and was independent of the degree of deformation in the cold-worked material.
In view of these and some other characteristics Stanley and Szkoipiak suggested that the relaxation mechanism causing the peak was the stress-induced ordering of vacancies associated with interstitial impurities. The associated activation energy of the relaxation process was estimated to be of the order of magnitude of about 12 kcal mol⁻¹ [209].

6. Concluding remarks. — The preceding review is hoped to give an up-to-date account of internal friction effects and the models used to interpret these effects in solids containing point defects. We have seen that, although in some cases the data is limited and fragmentary, in other cases the data is sufficiently complete so that one can plan further experiments to pin down specific problems. The main thing which clearly emerges from the review is that internal friction as an experimental technique provides useful, and in many cases unique, information on an atomic scale concerning the behaviour of point defects in solids.

It is hoped that future experimental efforts will be directed towards the studies of intrinsic point defects and substitutional-interstitial interacting effects in metals and alloys of technological interest. There is also a great need for further detailed studies of relaxation effects in the Group VIA, FCC and HCP metals containing interstitial impurities.

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