Internal Stresses in the $\alpha-\alpha'$ Phase Transition of Coherent Metal-Hydrogen Systems

Theodore W. Burkhardt*
Institut für Festkörperforschung, Kernforschungsanlage Jülich

Received May 9, 1974

Abstract. In an $\alpha-\alpha'$ phase transition of the type discussed by Wagner and Horner, the smoothly varying hydrogen distribution generates coherency stresses in the metal crystal. The system is in a metastable state, which is expected to have a long lifetime if the internal stresses are smaller than some critical stress for destroying coherency. A comparison of the calculated internal shear stress with the experimental value of the critical shear stress for the onset of plastic deformation in a Nb crystal suggests that there may well be an appreciable region in which a coherent transition is experimentally observable.

1. Introduction

Recently Wagner and Horner [1, 2] presented a theory of the $\alpha-\alpha'$ ("gas-liquid") phase transition [3, 4] of hydrogen dissolved in a completely coherent metal crystal. For a coherent niobium sample of spherical shape sealed so that the hydrogen content is constant the theory predicts the phase diagram shown in Fig. 1. Above the heavy solid line the hydrogen distribution in the sample is homogeneous. Below the line the hydrogen distribution varies smoothly on a macroscopic scale. There is a continuous transition between regions of high and low hydrogen density extending over the entire sample rather than an abrupt interface between $\alpha$ and $\alpha'$ phases. The formation of a sharp interface in a coherent crystal is energetically unfavorable because of the associated elastic energy.

Below the transition line the macroscopically-varying hydrogen density generates coherency stresses in the crystal. As discussed in [1], the system is in a metastable state. The incoherent state in which internal stresses have been relieved by the formation and motion of dislocations is the true equilibrium state. However, one expects the metastable state to have a long lifetime if the internal stresses due to the inhomogeneous hydrogen distribution are smaller than some critical stress for destroying coherency in the lattice. To estimate the size of the experimental region in which a coherent $\alpha-\alpha'$ transition should be observable, the

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* Alexander von Humboldt Fellow, on leave from Lincoln University, Pennsylvania 19352, U.S.A.
internal stress has been calculated and compared with the experimental value of the critical shear stress for the onset of plastic deformation in the host crystal. The results are reported below.

2. The Internal Shear Stress

Wagner and Horner consider a spherical, isotropic crystal of radius \( R \) with a hydrogen density \( \rho(r) \) symmetric about the \( z \) axis. They describe the hydrogen density by the first few terms in an expansion in macroscopic density modes.

\[
\rho(r) = \sum_{\ell=0}^{\infty} \rho_{\ell} \left[ (2\ell + 3) \frac{4\pi/3}{R} \right] Y_{\ell}(\theta).
\]

The \( \rho_{\ell} \) are temperature-dependent coefficients which vanish above the transition line; \( r, \theta, \) and \( \varphi \) are spherical coordinates; and the \( Y_{\ell}(\theta) \) are spherical harmonics. In the continuum approximation an explicit expression for the displacement field \( u(r) \) describing the distortion of the lattice due to the introduction of the hydrogen may be worked out with the help of Appendix B in [1].

\[
u(r) = R \sum_{\ell} \rho_{\ell} \left[ (\ell^2 + (\ell + 2) \ell + 1) \frac{r}{R} \right] Y_{\ell}(\theta) + \left[ \ell^2 - 3 \ell + 2 \right] RV \cdot Y_{\ell}(\theta)
\]

where \( \ell = r/R \)

\[
\rho_{\ell} = -2 \left[ (\ell^2 + \ell + 1) \mu + (2\ell^2 + 4\ell + 3) \lambda \right].
\]

Here \( 3P \) is the trace of the elastic dipole moment tensor and \( \lambda \) and \( \mu \) are the Lamé constants of the host lattice. The following spherical components of the strain tensor [5, 6] \( \epsilon_{\ell\ell} \) are obtained from the displacement field of Eq. (2):

\[
\begin{pmatrix}
\epsilon_{rr} \\
\epsilon_{\theta\theta} \\
\epsilon_{\varphi\varphi} \\
\epsilon_{\varphi\varphi}
\end{pmatrix} = \sum_{\ell} \rho_{\ell} \left[ (\ell^2 - 1) (\ell + 1) (\ell + 2) \right] \frac{r}{R} \left( \begin{array}{c}
(\ell - 1) \ell + (\ell + 1) (\ell + 2) \epsilon^2 \\
-\ell^2 + (3\ell^2 + 4\ell + 2) \epsilon^2 - (1-3\epsilon^2) \cot \theta \frac{\partial}{\partial \theta} \\
\ell + (\ell + 2) \epsilon^2 + (1-3\epsilon^2) \cot \theta \frac{\partial}{\partial \theta} \\
(\ell - 1)(1-\epsilon^2) \frac{\partial}{\partial \theta}
\end{array} \right) R Y_{\ell} \cdot \frac{\partial}{\partial \theta}
\]

\[
\epsilon_{\varphi\varphi} = 0.
\]

In terms of these spherical components the principle values or eigenvalues of the strain tensor are given by

\[
\begin{align*}
\epsilon_{1,2} &= \frac{1}{2} \{ \epsilon_{rr} + \epsilon_{\theta\theta} \pm \sqrt{(\epsilon_{rr} - \epsilon_{\theta\theta})^2 + 4\epsilon_{\varphi\varphi}^2} \} \\
\epsilon_{3} &= \epsilon_{\varphi\varphi}.
\end{align*}
\]

In an isotropic elastic continuum the shear components of the stress tensor \( \sigma_{\alpha\beta} \) and the strain tensor \( \epsilon_{\alpha\beta} \), resolved along perpendicular \( \alpha \) and \( \beta \) axes, are related by [5]

\[
\sigma_{\alpha\beta} = 2 \mu \epsilon_{\alpha\beta}.
\]

The magnitude of the shear stress depends on the orientation of the \( \alpha \) and \( \beta \) axes. If the axes are parallel to principal axes of the strain tensor, then the shear stress is zero, since the strain tensor resolved along its principal axes has only diagonal components. For any other orientation of the \( \alpha \) and \( \beta \) axes the shear stress is nonzero. Let the maximum, minimum, and intermediate eigenvalues of the strain tensor be denoted by \( \epsilon_{\text{max}}, \epsilon_{\text{min}}, \epsilon_{\text{int}} \). It is a well-known result [6] that the maximum shear stress occurs in the coordinate system obtained by rotating the principal axis system 45° about the principal axis corresponding to \( \epsilon_{\text{int}} \). The \( \alpha \) and \( \beta \) axes are the \( \epsilon_{\text{max}} \) and \( \epsilon_{\text{min}} \) axes after this rotation. The maximum shear stress is given by

\[
\sigma_{\text{shear}}^{\text{max}} = \mu |\epsilon_{\text{max}} - \epsilon_{\text{min}}|.
\]

With values of \( \rho_{\ell} (\ell = 0, \ldots, 5) \) calculated as in [2] and constants appropriate for Nb (3\( P = -10 \) eV, \( \mu/\lambda = 0.3 \)), \( \sigma_{\text{shear}}^{\text{max}} \) was calculated at various points in the spherical sample for a variety of hydrogen concentrations using Eq. (4), (5), and (7). Typical stress patterns are shown in Figs. 2 and 3. The indices labelling each smooth segment of the curve \( r = R \) in Fig 2 indicate which principal values of the strain tensor enter the maximum shear stress. For example 1, 2 means that \( \sigma_{\text{shear}}^{\text{max}} = \mu |\epsilon_{1} - \epsilon_{2}| \). The principle values \( \epsilon_{i} \) are smooth functions of position in the sample. The discontinuities in slope in Figs. 2 and 3 occur where the indices change, for example where \( \epsilon_{\text{max}} \) goes from \( \mu |\epsilon_{1} - \epsilon_{2}| \) to \( \mu |\epsilon_{1} - \epsilon_{3}| \).

In Figs. 2 and 3 one sees that the greatest shear stress in the sphere occurs at the surface on a ring \( \theta = \) constant. There are no \( \ell = 0 \) and \( \ell = 1 \) contributions to the shear stress, since no coherency strains are associated with a homogeneous hydrogen distribution or a hydrogen distribution with a constant gradient [1]. At the critical concentration (Fig. 2) the \( \ell = 3 \) contribution dominates and yields two peaks in the shear stress near the surface. The small \( \ell = 2 \) contribution produces the slight asymmetry about 90° in the shear stress at the surface. Away from the critical