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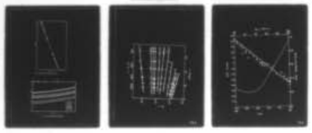

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FINAL REPORT

THERMODYNAMIC AND KINETIC PROPERTIES OF SOLUTE ATOMS IN INTERSTITIAL SOLID SOLUTIONS

Grant Number DAAG-29-78-G-0017

January 1, 1979

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Measurements of the elastic properties of the Group V metals from room temperature up to 2000°K have shown that the "lattice softening effect" is not responsible for non-Arrhenius behavior seen in the diffusion of interstitial atoms through these metals.

Work on the Fe-C and Pd-H systems has shown that the volume changes associated with the insertion of a solute atom has a second-order effect on the mobility of the interstitial solute, but has a significant effect on the thermodynamic properties. (OVER)

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The temperature variation of the H-solubility in a series of Mo-Nb solvents has been measured. The resulting enthalpies of solution show a variation with the electronic density of states at the Fermi surface which is not in accord with the screened proton model for H-metal systems.

The diffusivity of hydrogen in several noble metals has been measured using the permeability time-lag technique.

Statement of Problems

The problems outlined in the original proposal, and in fact investigated in the research work performed, all belong to the category of interstitial solid solutions. Both thermodynamic and kinetic effects in such systems have been investigated.

All the projects investigated are interrelated to a greater or lesser degree, but, for the sake of clarity, they may be classified into three general areas as follows:

A) Departures from nonlinearity in Arrhenius plots for the diffusion of interstitial atoms in bcc metals.

B) Volume effects in solid solutions. As the solute concentration in a solid solution is changed, the specific volume changes. This is a particularly important effect in interstitial solid soltuions, and the two most relevant problems center on the experimental measurement of these effects and secondly on their theoretical implications in the thermodynamic theory of solid solutions.

C) Electronic effects in hydrogen-metal systems. The theoretical models for hydrogen-metal systems indicate that there should be a relationship between the energy to dissolve a proton in the metal lattice and the electronic structure of the solvent metal. The problem in this area is to choose a metal binary solution "solvent" of known electronic structure and experimentally determine the thermodynamic functions of hydrogen in this solution.

Summary of Results

A. Non-Linear Diffusion

In many bcc-metal interstitial systems the plot of ln D vs. 1/T shows a positive deviation from linearity at high temperatures where the diffusion coefficient D becomes large. A series of papers have been written concerning the origin of such effects (see list of Publications appended). The best-documented example is the O-Nb system illustrated in Fig. (1). The open symbols were taken from mass-flow data and the solid symbols are taken from damping work. The lower line is an extrapolation of the linear plot of ln D vs 1/T found at low temperatures.

The suggestion had been often made that such behavior is due to the "softening" of the parent lattice at high temperatures. In the current work (paper 16) it has been shown that if the elastic moduli vary linearly with temperature, the activation energy for diffusion would remain invariant to temperature and the plot of ln D vs. 1/T should remain linear.

The deviations from Arrhenius behavior have been found in C, O, and N diffusing through the Group V metals. In order to test the "softening" hypothesis a UHV system was constructed which enabled a pulse-echo ultrasonic determination of the Young's modulus and shear modulus to be measured in V, Ta, and Nb up to temperatures approaching 2000°K. The measured data show no departure from linearity in the entire temperature range except for a small modulus-defect in the case of Nb. The temperature spans of the data are shown below

Metal	$\Delta T\,^{\circ}K$
Nb	273-1900
Ta	273-2100
V	273-1800

Although this work is essentially complete, the manuscript has not yet been completed since more work is being performed on the low-temperature modulus defect found in niobium.

It is likely that the explanation for the group V metals lies in the dual occupancy of both tetrahedral and octahedral sites in the bcc lattice (paper 3). If this is true, there should be the possibility of "seeing" this effect in the high-temperature thermodynamic properties. The thermodynamic equilibrium between N_2 gas and N-Mo solid solutions has been measured up to 2700°K. This system also shows a deviation in the diffusiion behavior. The thermodynamic data have been carefully analyzed and good evidence for simultaneous site occupation has been found (paper 10).

B. Volume Effects

In a diffusion couple with a concentration gradient, there is a concomitant gradient of specific volume due to the lattice dilation created by the interstitial atoms. The specific volume gradient causes the local diffusivity to depend on the concentration and the gradient strength. A theoretical analysis however (paper 5) shows that the effect is negligible for all reasonable gradients.

In most theoretical models for solid solutions volume changes are ignored. The energy of solution calculated in such models is in fact,

$$\tilde{E}_u = \left(\frac{\partial E}{\partial N_u}\right)_{V,T,N_v}$$

where E is the internal energy, N is the number of moles (V = solvent, U = solute), and T is the temperature. The problem arises in comparing $\tilde{E}_u$ (calculated) with $\bar{H}_u$, the measured partial enthaply of the solute. It has been shown in this work (paper 9) that the variation of $\tilde{E}_u$ and $\bar{H}_u$ with the atom ratio, $\theta = N_u/N_v$, is given by,

$$\left(\frac{\partial H_u}{\partial \theta}\right)_{P,T} - \left(\frac{\partial \tilde{E}_u}{\partial \theta}\right)_{V,T} = - \frac{(\bar{V}_u)^2}{V_s K} \Bigg[1 - T\alpha \Bigg[\frac{2}{\bar{V}_u \alpha} \left(\frac{\partial \bar{V}_u}{\partial T}\right)_P$$

$$-2 \left(1 + \frac{V_s}{\bar{V}_u K} \left(\frac{\partial K}{\partial \theta}\right)_{P,T} \right] + \frac{V_s}{(\bar{V}_u)^2} \left(\frac{\partial \bar{V}_u}{\partial \theta}\right)_{P,T} - \frac{1}{K\alpha} \left(\frac{\partial K}{\partial T}\right)_P \Bigg]$$

where $V_s = V/N_v$, $\bar{V}_u$ is the partial molar volume, K is the isothermal compressibility, and α is the thermal expansivity.

This equation has been applied to the case of carbon austinite with the result (paper 9), at $T = 1273^\circ K$,

$$\tilde{E}_u = \bar{H}_u - 27.5 + 206\ \theta + 4722\ \delta \quad \text{kJ/mol}$$

where $\delta = \ln (1 + 0.516\theta)$.

Now these results are interesting and relevant to the properties of Pd-H solutions. In this system $\bar{H}_u$ is found to vary at very low H-concentrations where direct H-H interactions would not be expected to affect $\bar{H}_u$. However, the variation is small. Since all the many previous measurements on the Pd-H system were made either at high H-concentrations or using polycrystalline Pd, it was decided to measure P-T-θ isobars using MARZ-grade single crystals of Pd. This work has been carried out (paper 8) and the results can be seen in Fig. (2). Each symbol refers to a different H_2 pressure. The analysis of the results confirm the $\bar{H}_u$-variation with θ in the concentration range $\theta = 0.01$ to 0.001. This effect has been ascribed to volume changes. The large temperature variation in $\bar{H}_u$ and $\bar{S}_u$ at a fixed concentration has been discussed in terms of several model proposals for

H-Pd solutions (paper 8).

C. Electronic Effects

The original proposal for this research called for measurements of the energy of solution of hydrogen in Mn-Cr binary solutions. During the planning of the experiments, however, it became apparent that the Mo-Nb system was more appropriate.

The reasons for this suitability may be listed as follows:

(1) The two bcc metals form a continuous series of solid solutions. The Goldschmidt radii of the two metals are very close, the Hume-Rothery size factor being only 4.7%.

(2) The electronic work functions ϕ of the two metals are virtually identical. ϕ has been measured by the thermionic, photoelectric, and contact potential difference method for Mo. The three methods give excellent mutual accord and the mean value is 4.32 e.V. This value is close to the value of 4.37 e.V. determined for Nb by the contact potential difference method.

(3) The variation of N(E) with concentration for binary Mo-Nb solutions is well-known. The calculated values are in excellent accord with the measurements of the Hall effect coefficient. The Hall effect coefficient exhibits a large peak in the region between 5.75 and 5.93 outer electrons per atom, which corresponds to the minimum in the N(E) curve at 5.8 outer electrons per atom (e/A). Furthermore measurements of the variation of the resistivity with composition yield a curve which is parallel to the N(E) curve.

(4) The N(E) varies rapidly with composition. As Mo is added to Nb, N(E) decreases rapidly by about an order of magnitude, reaching a minimum

at ∿5.8 e/A and the slowly increasing to its value for pure Mo.

The solubility of H has been measured in 11 Nb-Mo solid solutions as a function of temperature. The data are shown in Fig. (3). The values of $\Delta\bar{H}_i$, the relative partial enthalpy of solution, are plotted against the electron/atom ratio in Fig. (4). The present data are shown by the symbols Φ and the other symbols refer to different investigators. The curved line showing the pronounced minimum at ∿5.75 e/A is the N(E) curve.

The screened proton model predicts that $\Delta\bar{H}_i$ would change drastically concomitant to the 5-fold change in N(E) as the Nb/Mo ratio is changed. This is clearly not the case. Furthermore there is no sign of an extremum in the variation of $\Delta\bar{H}_i$ with Nb/Mo ratio as would be predicted from the shape of the N(E)-curve.

It should be stressed again that he Nb-Mo-H system was selected because the changes in work function and "strain energy" effects on passing from Nb to Mo are expected to be small in relation to the energy change corresponding to the large change in N(E) computed in the screened proton model.

On the basis of the current results on previous investigations of ternary H-metal systems (Fe-Ni-H and Fe-Cr-H), it must be concluded that the thermodynamic studies on ternary solutions do not support the screened proton model.

However the correlations which have been found between the $\Delta\bar{H}_i$-values for many binary solutions and the temperature coefficient of the electronic specific heat, provide some support of the theory. This is not understood by the present author. It is his belief that the rather large volume of thermodynamic data which has been amassed in the last ten years for H-metal solutions can provide a basis of comparison for the theoretical models, but these models seem to be at a stage of development where uncertainties in predicted values of $\Delta\bar{H}_i$ are much larger than the range of variations in measured $\Delta\bar{H}_i$ values. The experimental work performed on the Nb-Mo-H system had been written up and the manuscript is currently under review (Acta Metallurgica).

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In addition to the projects discussed in this report, several other subsidiary projects have been completed. They may be listed as follows:

a) Statistical mechanical treatment of H-Group V solutions. The quasi-free nature of the H-atoms in the metal lattice has been considered (papers 1 and 2).

b) An investigation of the thermodynamics of the H-Mn system (paper 4).

c) A first-order treatment of the kinetics and thermodynamics of ternary solutions (paper 7).

d) A series of studies on the kinetics of hydrogen in the noble metals (papers 11, 12 and 13).

Publications

The Research undertaken has resulted in the following publications:

(1) R. B. McLellan, "A Statistical Mechanical Model for Solid Solutions of Hydrogen in Niobium, Vanadium, and Tantalum," J. Phys. Chem. Solids, 37, 433 (1976).

(2) J. R. da Silva and R. B. McLellan, "Thermodynamic Functions of H in the Group V Metals," J. Mats. Sci. Eng., 24, 137 (1976).

(3) J. R. G. da Silva and R. B. McLellan, "The Diffusivity of Carbon and Nitrogen in bcc Iron," J. Mats. Sci. Eng., 26, 83, (1976).

(4) J. R. da Silva and R. B. McLellan, "The Managanese-Hydrogen System," J. Mats. Sci. Eng., 27, 101 (1977).

(5) R. B. McLellan, "Interstitial Diffusion in a Chemical Gradient," J. Phys. Chem. Solids, 38, 933 (1977).

(6) R. B. McLellan, "Diffusivity of Carbon in Molybdenum," J. Mats. Sci. Eng., 28, 161 (1977).

(7) R. Farraro and R. B. McLellan, "Thermodynamic and Kinetic Properties of Ternary Solutions," Acta Met., 25, 1217 (1977).

(8) C. Labes and R. B. McLellan, "Thermodynamic Properties of Dilute Palladium-Hydrogen Solid Solutions," Acta Met., 26, 893 (1978).

(9) R. B. McLellan, "Volume Effects in Iron-Carbon Solid Solutions," Scripta Met., 12, 345 (1978).

(10) R. B. McLellan and R. J. Farraro, "Thermodynamics of Molybdenum-Nitrogen Solid Solutions," Acta Met., 26, 1727 (1978).

(11) W. M. Yei and R. B. McLellan, "Partial Thermodynamic Functions of Hydrogen in Platinum." Accepted in J. Less-Common Metals.

(12) H. Katsuta and R. B. McLellan, "Diffusivity of Hydrogen in Palldium." Accepted in Acta Met.

(13) H. Katsuta and R. B. McLellan, "Diffusivity, Permeability and Solubility of Hydrogen in Platinum." Accepted in J. Phys. Chem. Solids.

Two other manuscripts are currently being prepared.

Participating Scientific Personnel

1) Rex B. McLellan, Principal Investigator

2) Raymond Farraro, Graduate Student

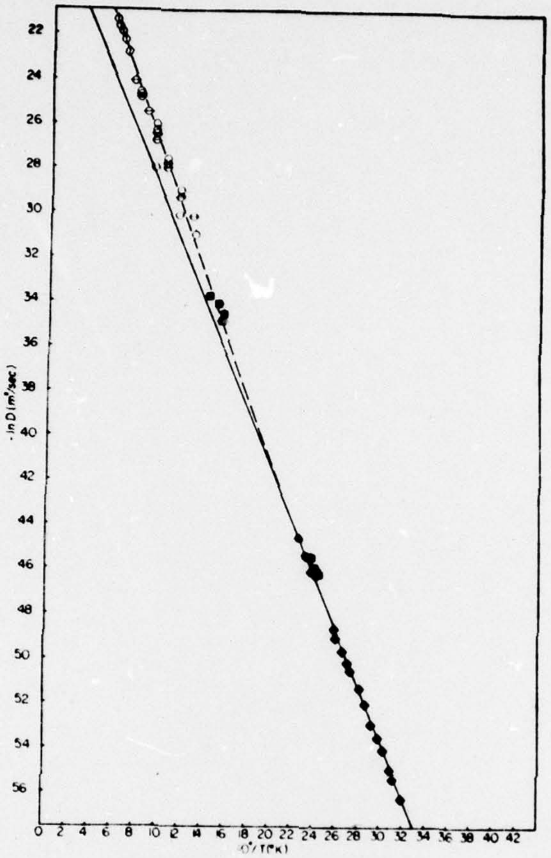

Fig. 1. Diffusivity of oxygen in niobium.

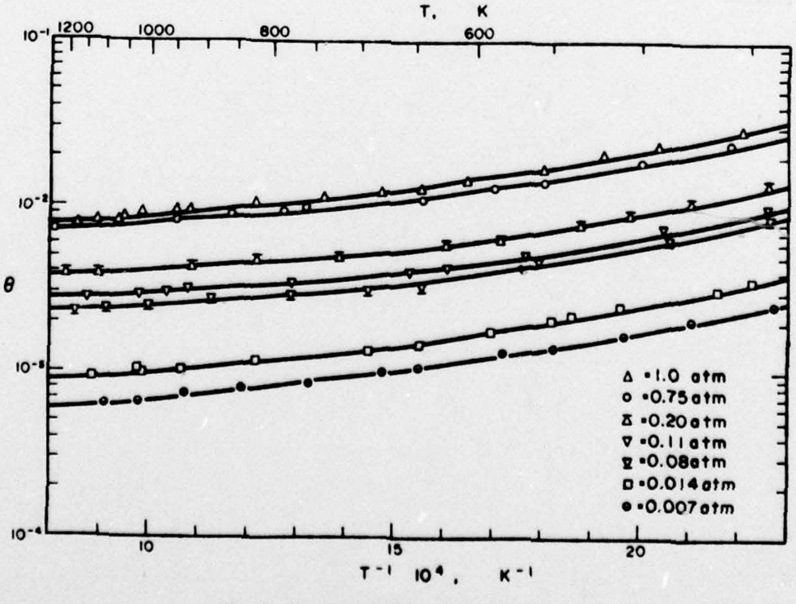

Fig. 2. Experimentally determined isobars.

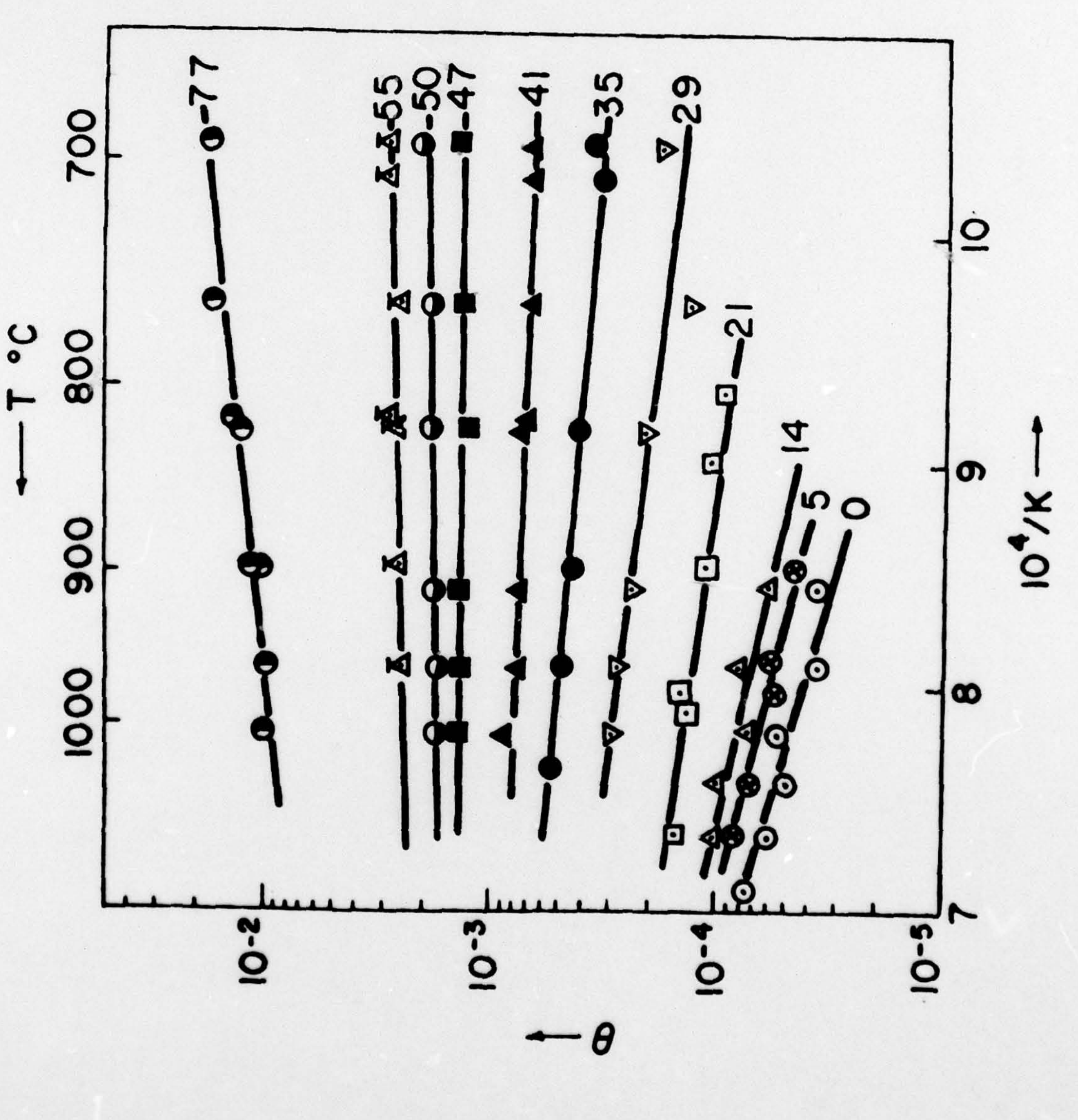
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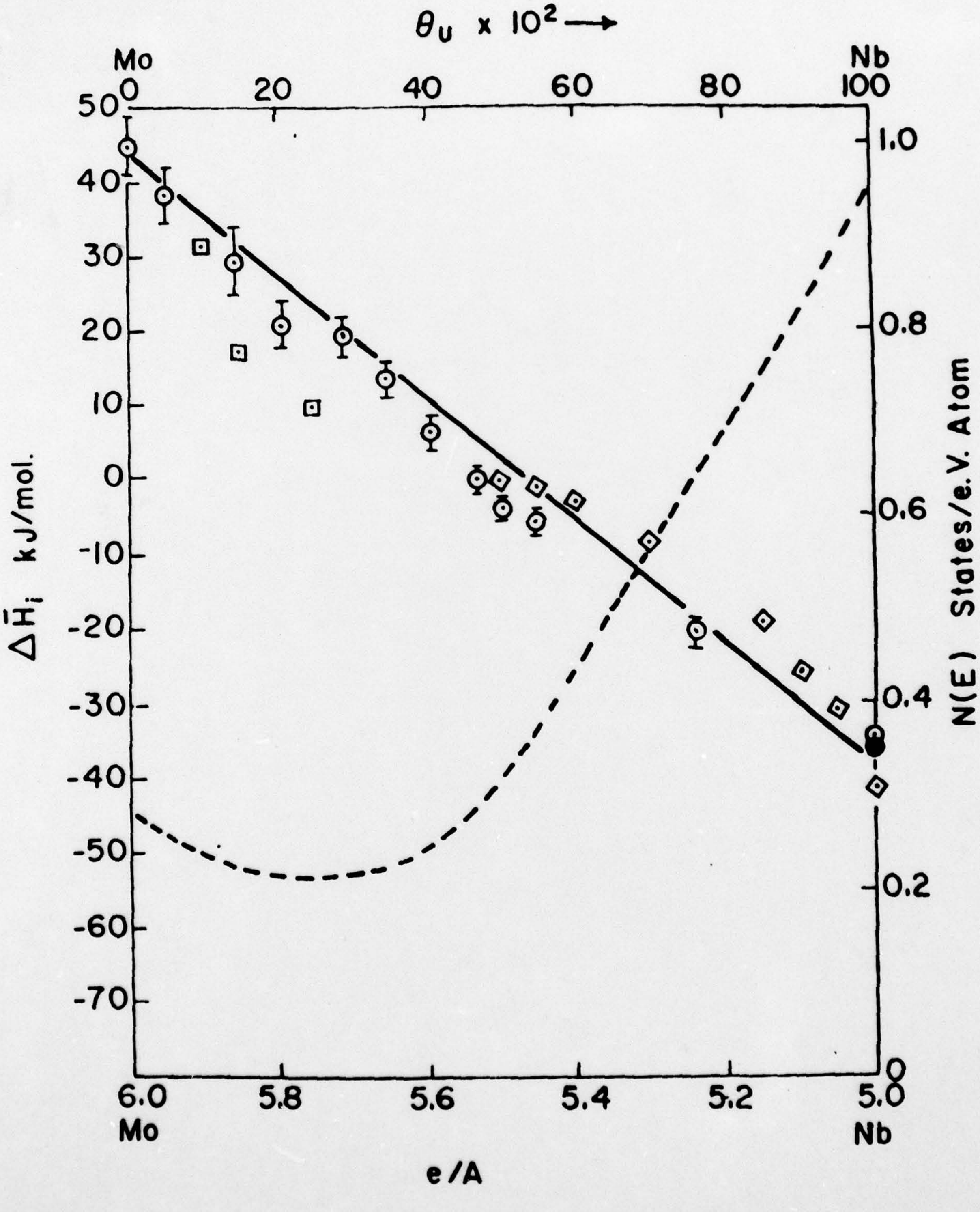
Fig. 3

 θ_u x 10^2 ⟶
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-60
-70
$\Delta\bar{H}_i$ kJ/mol.
1.0
0.8
0.6
0.4
0.2
0
N(E) States/e.V. Atom
6.0
5.8
5.6
5.4
5.2
5.0
Mo
Nb
e/A

Fig.4