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Neutron Diffraction Study of Temperature-Dependent Properties of Palladium Containing Absorbed Hydrogen

G. A. FERGUSON, JR.*
The Catholic University of America, Washington, D. C. and
U. S. Naval Research Laboratory, Washington, D. C.

AND

A. I. SCHINDLER
U. S. Naval Research Laboratory, Washington, D. C.

AND

T. TANAKA AND T. MORITA
The Catholic University of America, Washington, D. C.

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Neutron diffraction techniques have been employed to study the hydrogen-atom configuration in a single-phase sample of beta-PdH at several selected temperatures. The suggested low-temperature ($T<<55$°K) structure of this compound is one which conforms to the space group $R\bar{3}m$, which differs from the high temperature ($T>>55$°K) structure [$Fm3m$]. The low-temperature structure is formed by a partial migration of hydrogen atoms from octahedral to nearby tetrahedral crystallographic sites in the face-centered cubic palladium lattice. Approximate values of the root-mean-square vibrational amplitude of the hydrogen atoms have been determined to be 0.25 Å ($T=293$°K) and 0.17 Å ($T=4.2$°K). The anomalous behavior observed in measurements of the temperature dependence of the electrical resistivity and heat capacity of this compound is explained by the transfer of the hydrogen atoms between the lattice sites.

INTRODUCTION

THE behavior of palladium containing absorbed hydrogen has been a subject of continued study because of the unusual diffusion properties of the gas in the metal. It has been determined[1] that when a palladium specimen is loaded with hydrogen two resultant phases may exist. These phases, designated as the α and β phase, are distinguished by the lattice parameter of the crystallographic unit cell. X-ray diffraction studies[2] at room temperature have shown the structure of both phases to be face-centered cubic. At very low hydrogen concentrations only the α phase is observed and it has a lattice parameter of 3.89 Å; as the hydrogen concentration is increased, the lattice is expanded and the β phase appears having a lattice parameter of 4.02 Å. Single β-phase samples are obtained when the H/Pd ratio exceeds 0.60. No evidence of intermediate values of the lattice parameter has been found.

The hydrogen atoms have been shown[3] to be localized at the octahedral positions of the palladium lattice in specimens for which $\mathrm{H/Pd}=0.706$ and $T\approx 293$°K. Schindler *et al.*[4] have measured the low temperature dependence of the electrical resistivity of samples of β-PdH for which $\mathrm{H/Pd}=0.6$ and have found an anomalous behavior at 43°K. A similar anomalous behavior near this temperature has been observed in measurements of the heat capacity of β-PdH by Aston and his coworkers.[5] To explain these anomalies, we have used the techniques of neutron diffraction to study the change in the hydrogen configuration of β-PdH at low temperatures.

EXPERIMENTAL METHOD

Standard procedures were employed to obtain neutron diffraction patterns from a powdered specimen of β-PdH at the temperatures 293, 77, and 4.2°K. The neutron source used was the uranium core of the Naval Research Reactor. The specimen was made by hermetically sealing a compressed cylinder of pure powdered palladium in a quartz ampoule which contained two small-diameter quartz tubes used for subsequent charging of the specimen with hydrogen. The ampoule containing the sample was evacuated and heated for several hours at 400°C. The sample rapidly absorbed the purified hydrogen gas which was admitted through one of the above-mentioned small-diameter tubes. When fully charged, the ampoule was sealed by closing these tubes with an oxy-hydrogen torch. The specimen was placed in a Dewar flask which, in turn, was mounted upon the goniometer table of the neutron diffractometer for analysis.

RESULTS OF MEASUREMENTS

The room-temperature neutron diffraction pattern of the β-PdH specimen, together with that from pure

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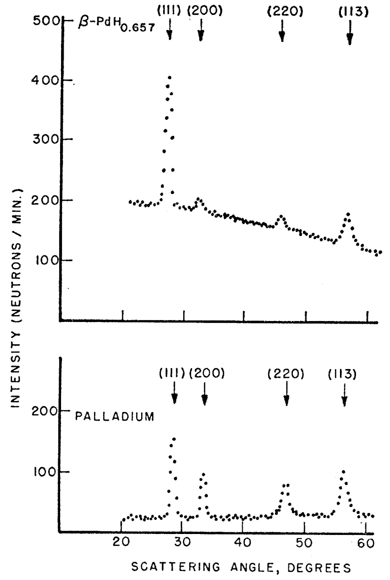

FIG. 1. Neutron diffraction spectra of PdH$_{0.657}$ and pure palladium at room temperature.

palladium (obtained for comparison), is shown in Fig. 1. The diffraction pattern of the pure palladium is that which is characteristic of a simple face-centered cubic lattice, while the diffraction pattern of the β-PdH specimen is representative of the Na-Cl type structure, [*Fm*3*m*], with the hydrogen atoms occupying the octahedral positions in the palladium lattice. For the β-PdH specimen at 293°K, we take the structure amplitude for even and odd (*hkl*) reflections to be

$$F(hkl)=4[f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}+(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2}],\quad (hkl)\ \text{even},\qquad (1)$$

$$F(hkl)=4[f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}-(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2}],\quad (hkl)\ \text{odd},\qquad (2)$$

where $f_{\rm Pd}$ and $f_{\rm H}$ are the neutron scattering amplitudes of palladium and hydrogen, respectively, and

$$b_{\rm Pd}=8\pi^2\bar{\mu}_{\rm Pd}^2;\quad b_{\rm H}=8\pi^2\bar{\mu}_{\rm H}^2.$$

The mean-square vibrational amplitudes of the palladium and hydrogen atoms in the solid are $\bar{\mu}_{\rm Pd}^2$ and $\bar{\mu}_{\rm H}^2$. A plot of the measured values of F(even) and F(odd) against $\sin\theta/\lambda$ gives two curves from which we may obtain

$$[F(\text{even})-F(\text{odd})]=8(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2},\qquad (3)$$

$$[F(\text{even})+F(\text{odd})]=8f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2},\qquad (4)$$

for each value of $\sin\theta/\lambda$. Values of the difference given in Eq. (3) and the sum given in Eq. (4) were plotted against $\sin^2\theta/\lambda^2$ on a semilogarithmic plot yielding straight lines of slope $b_{\rm H}(b_{\rm Pd})$ with intercepts $8(\mathrm{H/Pd})f_{\rm H}(8f_{\rm Pd})$. [These straight lines indicate that the thermal motion of the atoms may be considered isotropic.] This analysis gives

$$f_{\rm Pd}=0.60\times10^{-12}\ \text{cm},$$
$$(\bar{\mu}_{\rm H}^2)^{1/2}=0.25\times10^{-8}\ \text{cm},$$
$$(\bar{\mu}_{\rm Pd}^2)^{1/2}=0.104\times10^{-8}\ \text{cm},$$

and is in good agreement with earlier observations.[3] We take the well-known[6] scattering length of hydrogen $f_{\rm H}$ to be -0.38×10^{-12} cm, together with the measured value

$$8(\mathrm{H/Pd})f_{\rm H}=2\times10^{-12}\ \text{cm}$$

to obtain H/Pd = 0.657 for our sample.

Neutron diffraction measurements were also made at specimen temperatures of 77 and 4.2°K. The measured intensities at all temperatures are given in Table I for comparison. The fact that the neutron intensities did not show the expected monotonic change as the temperature was lowered below 77°K, together with the known anomalous behavior of the heat capacity and electrical resistivity, led to a search for a change in crystal structure.

In order to interpret the data obtained at a sample temperature of 4.2°K, we offer the following explanation. The structure of β-PdH is altered as the temperature is lowered below 55°K. This alteration consists of a migration of hydrogen atoms from octahedral sites (with coordinates $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) in the Na-Cl structure to nearby tetrahedral sites. A small distortion of the cubic palladium lattice would render the equivalent tetrahedral positions in the unit cell (with coordinates $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$) as preferred sites for the migrating hydrogen atoms. We give below the appropriate structure factors (based on the $R\bar{3}m$ space group) used to calculate the intensities of the measured reflections.

$$\begin{aligned}
F(111)&=4f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}-(4-y)(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2},\\
F(200)&=4f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}\\
&\quad+(4-2y)(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2},\\
F(220)&=4f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}+4(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2},\\
F(113)&=4f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}\\
&\quad-(4-y)(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2},\\
F(222)&=4f_{\rm Pd}e^{-b_{\rm Pd}\sin^2\theta/\lambda^2}\\
&\quad+(4-2y)(\mathrm{H/Pd})f_{\rm H}e^{-b_{\rm H}\sin^2\theta/\lambda^2},\qquad (5)
\end{aligned}$$

where y is the number of hydrogen atoms at tetrahedral sites.

Using the observed value of $F(111)$ at $T=4.2$°K we have determined the parameter y to be approximately 0.95. This, of course, implies that three of the hydrogen atoms have remained at their original octahedral sites. The values of the root-mean-square vibrational amplitudes of the atoms, $(\bar{\mu}^2)^{1/2}$, at this temperature, were obtained by using an analysis similar to that previously

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[6] J. E. Worsham *et al.* (Ref. 3); J. Bergsma and J. A. Goedkoop (Ref. 3); and G. E. Bacon, *Neutron Diffraction* (Clarendon Press, Oxford, 1955).

discussed. These are given in Table II, together with the structure factors determined from the measured relative intensities and those calculated for this model. The agreement is considered satisfactory. At a temperature of 4.2°K (which is far below the transition temperature of 55°K), the β-PdH system should be in its ground state. In this state, entropy considerations require the formation of a superlattice of hydrogen atoms which would render the available tetrahedral positions in adjacent unit cells as nonequivalent. This superlattice would be constructed by an ordered arrangement of hydrogen atoms in the available tetrahedral sites. The coherent intensities from this lattice, together with the intensities of the (100)—and (110)—reflections (forbidden for the cubic *Fm*3*m* structure but allowable for the $R\bar{3}m$ structure), were computed to be below the sensitivity of our instrument to isolate from the large spin incoherent scattering of the hydrogen atoms.

The root-mean-square vibrational amplitude obtained for the hydrogen atoms ($T=293$°K) was found to be considerably higher than the value obtained for the palladium atoms (compare 0.25 Å for H atoms and 0.104 Å for Pd atoms). These results are interpreted as being due to the weaker binding of the protons at high temperatures. As the specimen temperature is lowered ($T \ll 50$°K) the Pd-H coupling is strengthened by the formation of the $R\bar{3}m$ structure. To support this model, we have made neutron transmission measurements on our β-PdH specimen, and our results are given in Table III. These data indicate that the scattering cross section of hydrogen increases monotonically as the sample temperature is lowered. This behavior is consistent with the view that the hydrogen atoms are more strongly bound at low temperature. [σ(free) = 20 b, σ(bound) = 80 b.]

TABLE I. Measured intensities for β-PdH.

Reflection	Intensities $T=293$°K	 77°K	 4.2°K
(111)	1939	2330	1900
(200)	261	325	351
(220)	271	337	199
(113)	1084	1300	1215
(222)	152	180	169

TABLE II. Calculated and measured values of $F(hkl)$ for β-PdH at $T=4.2$°K. $(\bar{\mu}_{Pd}^2)^{1/2}=0.08$ Å; $(\bar{\mu}^2)^{1/2}=0.17$ Å; $y\equiv$number of H atoms at tetrahedral sites per unit cell$=0.95$.

Reflection	Structure factor Calculated	 Observed
(111)	3.05	3.07
(200)	1.80	1.75
(220)	1.49	1.33
(113)	2.65	2.59
(222)	1.80	1.72

DISCUSSION OF RESULTS

We now propose an explanation of the anomalous temperature dependence observed in measurements of the specific heat and resistivity of β-PdH samples. This explanation is based on the crystalline model described above.

Matter is known to condense into such states as will minimize the free energy

$$F=U-TS.$$

At low temperatures the internal energy U is dominant, whereas at high temperatures the term TS predominates. We suggest that for the β-PdH system the vibrational entropy takes the principal role in the observed change in the region of 55°K.

In order to understand how this vibrational entropy affects the behavior of the specific heat, let us assume a system composed of cells and that two structures, A and B, are possible for each cell. Let us further assume that the ground state free energy is lowest when all cells are of structure A. When all cells are of structure B, we assume the sound velocity to be lowest. For a mixed state containing A- and B-type structures, we take the ground-state energy $\bar{U}$ to be given by

$$\bar{U}=\bar{U}_A\rho_A+\bar{U}_B\rho_B=\bar{U}_A+N\rho_B\Delta u, \qquad (6)$$

where the populations $\rho_A(=N_A/N)$ and $\rho_B(=N_B/N)$ refer to structures A and B, respectively, and

$$\Delta u=(\bar{U}_B-\bar{U}_A)/N.$$

Under the assumption that the sound velocity c is a linear function of the cell population we write

$$c=c_A\rho_B+c_B\rho_B=c_A-\rho_B\Delta c, \qquad (7)$$

where $\Delta c=c_A-c_B$. The free energy is given by[7] $F=$ (internal energy) − (vibrational energy) − T ("mixing entropy"). Thus,

$$F=\bar{U}_A\rho_A+\bar{U}_B\rho_B+(9kT^4/\theta_D^3)8N\int_0^{\theta_D/T} y^2\ln(1-e^{-y})dy$$
$$+NkT[\rho_A \ln\rho_A+\rho_B \ln\rho_B], \qquad (8)$$

where θ_D is the Debye temperature. For low tempera-

TABLE III. Neutron transmission through β-PdH.

Temperature (°K)	σ scattering (10^{-24} cm^2)
293	31
77	35.5
4.2	37.7

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[7] See for example, F. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Oxford University Press, Cambridge, 1949).

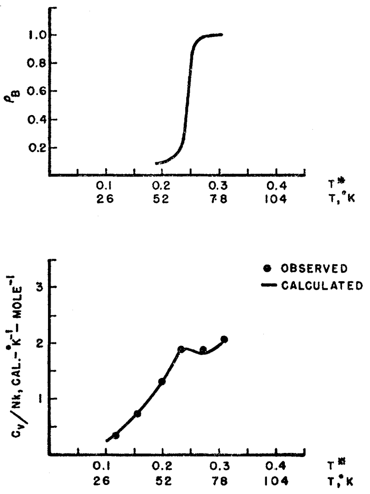

FIG. 2. Variation of ρ_B and c_v/Nk with T^*.

tures, i.e., $T \ll \theta_D$, we may obtain

$$F=\bar{U}_A\rho_A+\bar{U}_B\rho_B+NkT[\rho_A \ln\rho_A+\rho_B \ln\rho_B]$$
$$-3kT(8N)\left\{(\pi^4T^3/15\theta_D{}^3)-3\frac{T}{\theta_D}e^{-\theta_D/T}-\frac{6T^2}{\theta_D{}^2}e^{-\theta_D/T}-\frac{3T^3}{\theta_D{}^3}-0\left(\frac{T}{\theta_D}e^{-2\theta_D/T}\right)\right\}. \quad (9)$$

Define

$$T^*=NkT/(\bar{U}_A-\bar{U}_B)=kT/\Delta u, \quad (10)$$

and

$$\theta_D=\frac{h}{k}\left(\frac{3N}{4\pi v}\right)^{1/3} \quad c=\frac{h}{k}\left(\frac{3N}{4\pi v}\right)^{1/3}(c_A\rho_A+c_B\rho_B). \quad (11)$$

Then

$$\frac{F}{NkT}=\left[\frac{\bar{U}_A}{N\Delta u}+\rho_B\right]\frac{1}{T^*}+[(1-\rho_B)\ln(1-\rho_B)+\rho_B \ln\rho_B]$$
$$-3\left\{\frac{\pi^4}{15}\left(\frac{1}{kH}\frac{\Delta u}{\Delta c}\right)^3\left[8T^{*3}\Big/\left(\frac{c_A}{\Delta c}-\rho_B\right)^3\right]+\cdots\right\}, \quad (12)$$

where $H=(h/k)(3N/4\pi v)^{1/3}$. The value of ρ_B is to be determined by the condition of minimum free energy, i.e.

$$\frac{\partial}{\partial\rho_B}(F/NkT)=0, \quad (13)$$

or

$$\frac{1}{T^*}+\ln\rho_B-\ln(1-\rho_B)-3\left\{\frac{\pi^4}{15}\left[3\Big/\left(\frac{c_A}{\Delta c}-\rho_B\right)^4\right]\frac{5T^{*3}}{3\pi^4\tau^4}+\cdots\right\}=0, \quad (14)$$

where

$$\tau^{-4}=(\pi^2/10h^3)(8V/N)(\Delta u/\Delta c)^3.$$

With this requirement, we may obtain the energy E by

$$\frac{E}{N}=\left[\frac{\partial(F/NkT)}{\partial(1/kT)}\right]_{\rho_B} \quad (15)$$

or

$$\frac{E}{N\Delta u}=\left[\frac{\partial(F/NkT)}{\partial(1/T^*)}\right]_{\rho_B}\cong\rho_B+\frac{T^{*4}}{\tau^4}\cdot\left(\frac{c_A}{\Delta c}-\rho_B\right)^{-3}, \quad (16)$$

and the specific heat may be calculated by

$$\frac{c_v}{Nk}=\frac{\partial(E/N)}{\partial(kT)}=\left[\frac{\partial(E/N\Delta u)}{\partial T^*}\right]_{\rho_B}+\left[\frac{\partial(E/N\Delta u)}{\partial\rho_B}\right]_{T^*}\frac{\partial\sigma_B}{\partial T^*}, \quad (17)$$

where the value of $\partial\rho_B/\partial T^*$ is to be obtained by differentiating Eq. (14). The result is

$$\frac{c_v}{Nk}\approx\frac{4T^{*3}}{\tau^4}\frac{1}{(c_A/\Delta c-\rho_B)^3}+\left\{\frac{1}{T^*}+\frac{T^{*3}}{\tau^4}\left[3\Big/\left(\frac{c_A}{\Delta c}-\rho_B\right)^4\right]\right\}^2\Big/\left\{\frac{1}{\rho_B}+\frac{1}{1-\rho_B}+\frac{T^{*3}}{\tau^4}\left[4\Big/\left(\frac{c_A}{\Delta c}-\rho_B\right)^5\right]\right\}. \quad (18)$$

We have plotted in Fig. 2 the predicted variation of ρ_B with T^* [determined by Eq. (14)] for the following choice of parameters:

$$\tau^4=10^{-5},$$
$$c_A/\Delta c=5.39.$$

The value of τ^4 was chosen to obtain agreement between theory and experiment while the value of $c_A/\Delta c$ was obtained from an analysis of the heat-capacity data.[5] This analysis consisted of a determination of θ_D for

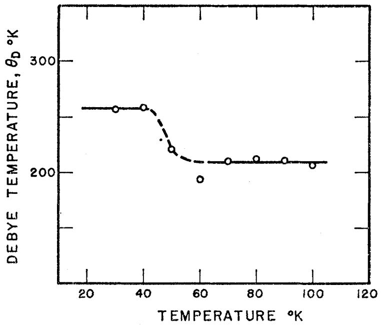

FIG. 3. Debye temperature θ_D versus T°K.

each value of the measured heat capacity by

$$\frac{c_v}{Nk}=9\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4e^x dx}{(e^x-1)^2}. \qquad (19)$$

These values are plotted in Fig. 3. We have determined c_B from the average value of θ_D above $T=50$°K and c_A from the average value of θ_D below this temperature by Eq. (11). We have also shown, in Fig. 2, the agreement obtained between the observed and the calculated values of c_v/Nk.

The anomaly observed in the electrical resistivity[4] may now be interpreted as arising from the increased electronic scattering produced by the disordered arrangement of the hydrogen atoms among octahedral and nearby tetrahedral sites in the palladium lattice. The significantly larger value of the resistivity observed at 4.2°K for β-PdH above that measured for either α-PdH or pure palladium is due to the difference in electron conduction through the lattice of lower symmetry.

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Change of Mean Phonon Occupation Numbers in a Cubic Crystal During Adiabatic Compression

T. H. K. Barron*
Division of Pure Physics, National Research Council, Ottawa, Canada
and
Department of Physical Chemistry, University of Bristol, Bristol, England

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It is shown that during an infinitesimal adiabatic compression the average number of phonons $\bar{n}_j$ in a normal mode of a solid changes by an amount

$$d\bar{n}_j=\{(\gamma_j-\gamma)c_jT/\hbar\omega_j\}d\ln V,$$

where ω_j is the angular frequency of the mode, c_j its contribution to C_V, $\gamma_j=-d\ln\omega_j/d\ln V$, and γ is the Grüneisen function $\beta V/\chi_S C_P$ (derived from the volume coefficient of expansion β, the adiabatic compressibility χ_S, and the heat capacity at constant pressure C_P).

When calculating anharmonic contributions to adiabatic elastic constants, Stern[1] and Leibfried and Ludwig[2] assumed that

$$C_{\alpha\beta\gamma\delta}{}^{\mathrm{ad}}\equiv(\partial^2E/\partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta})_S=(\partial^2E/\partial\eta_{\alpha\beta}\partial\eta_{\gamma\delta})_{\bar{n}_j}, \qquad (1)$$

where E is the internal energy, S is the entropy, the $\eta_{\alpha\beta}$ are Lagrangian strain coordinates, and the $\bar{n}_j$ are the mean phonon occupation numbers; $\bar{n}_j$ is defined as the average number of phonons in the jth normal mode. As we shall see, this assumption is only valid provided that there are no nonvibrational contributions to C_V, and provided that we make the approximation (used both by Stern and by Leibfried and Ludwig) that $d\ln\omega_j/d\ln V$ is the same for all normal frequencies ω_j; in general, the assumption is invalid. According to the quasiharmonic approximation, the vibrational entropy of a crystal is indeed a function only of the $\bar{n}_j$; but this does not mean that during an adiabatic process the $\bar{n}_j$ will necessarily remain constant. There will usually be an exchange of entropy between different parts of the vibrational spectrum; and for solids with nonvibrational contributions to the entropy (e.g., from conduction electrons) there may also be an exchange of entropy between the lattice vibrations and the nonvibrational systems.

For a cubic crystal, both these effects can be taken into account by means of the Grüneisen function $\gamma(T,V)$. This function is widely used in the interpretation of thermal expansion measurements, and is usually defined by

$$\gamma=\beta V/\chi_S C_P=\beta V/\chi_T C_V, \qquad (2)$$

where β is the volume coefficient of expansion and χ_S is the adiabatic compressibility.[3,4] Its importance for adiabatic compression can be seen from the thermodynamically equivalent definitions

$$\gamma=(\partial S/\partial\ln V)_T/C_V \qquad (3)$$

$$=-(\partial\ln T/\partial\ln V)_S. \qquad (4)$$

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* Permanent address: Department of Physical Chemistry, University of Bristol, Bristol, England.

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