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Effective and Debye temperatures of Ti in TiC, TiO_2, and TiH_2

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The relative intensities of resonantly scattered gamma rays by ^{48}Ti, at room and liquid-nitrogen temperatures, were measured in TiC, TiO_2, and TiH_2 with use of the nuclear-resonance photon-scattering technique. The results enable determination of the effective temperature T_e and the Debye temperature Θ_D of Ti in the various compounds with assumption of the Debye model. A significant increase in T_e and Θ_D of the Ti atoms was observed in TiC and TiO_2, while no detectable change in T_e and Θ_D was observed in pure Ti upon hydrogenation. The present results are discussed and compared with data obtained by other techniques.

I. INTRODUCTION

The first application of nuclear-resonance photon scattering (NRPS) for the study of Debye temperatures of pure metallic solids, Ni and Pb, was carried out several years ago.[1] The same technique was later applied to the study of the effective temperature of nitrogen occurring in various chemical forms such as $LiNO_3$, BN, and NH_4Cl. A theoretical treatment accounting for the binding forces acting on the N atom was developed, thus predicting correct values of T_e.[2,3] More recently, the same experimental method was used for studying Θ_D in metal hydrides.[4] An empirical correlation between the relative change of Θ_D upon hydrogenation and the hydride heat of formation has been consequently derived.[5,6] A careful examination of the data utilized in deriving the above empirical rule received some ambiguity in the interpretation of the experimental results by various authors.[6] The ambiguity occurred because some authors have ignored while others have included the H atoms in deriving Θ_D from low-temperature heat-capacity and elastic measurements.

It may be noted that in a diatomic metal-hydrogen linear lattice with nearest-neighbor interactions only, the metal atoms contribute to the lower-energy acoustic phonons while the H atoms contribute to the higher-energy optical phonons. At low temperatures only the acoustic modes are excited and, probably due to this, some authors have taken into account the metal atoms only in deriving Θ_D. Of course, the actual situation in metallic hydrides is much more complicated and examples were reported, e.g., $LaNi_5H_6$, NbH_x, and TaD_x, where the H excitations were within the host lattice modes and far below the local H vibrational energies.[7-9] It should be emphasized that the present technique is unique in two respects. First, it monitors the bonding strength of a single element (through both Θ_D and the effective temperature, T_e, defined below) in any chemical compound. Second, it is sensitive to the zero-point vibrational energies of the atomic oscillators occurring in the compound. This means that the high-energy vibrational modes will have an important contribution at all temperatures. From the above it also follows that the value of Θ_D obtained will be usually equivalent to the high-temperature limit of Θ_D obtained by other methods. Some difficulties may arise in defining Θ_D of a single element in a chemical compound and the subsequent derivation of T_e from the present experimental data: only relative measurements at different temperatures were made and the assumption of the Debye model, necessary for deriving Θ_D and T_e, should be justified. This justification is especially required here, where mixtures of light and heavy atoms are considered.

In the present work, we were primarily interested in the study of Θ_D of Ti in $TiH_{1.85}$. The study of TiC and TiO_2 was motivated by the need of selecting a Ti compound which is expected to yield a value of Θ_D distinctly different from that of the pure metal. In addition, some ambiguity concerning the interpretation of Θ_D was reported in the literature concerning some interstitial compounds which include TiC.[10] Some of the results presented here have been mentioned in a previous publication.[11]

II. EXPERIMENTAL METHOD

Experimentally, we used a photon beam generated from the $V(n,\gamma)$ reaction using thermal neutrons from the Israel Research Reactor (IRR-2). The source was in the form of six separated vanadium discs, placed along a tangential beam tube and near the reactor core yielding typical intensities of $\sim 10^5$ photons/cm^{2}s per strong γ line at the scatterer. This photon source contained several discrete γ lines, Doppler broadened by the thermal motion of the V atoms. The temperature of the vanadium discs during reactor operation was 600 K. More details on the experimental system may be found elsewhere.[12] In the present measurements, we utilized the accidental overlap between one of the incident γ lines at 6605 keV with a nuclear level in the ^{48}Ti isotope.[13] This overlap gives rise to a resonance scattering signal whose cross section σ_s is proportional to the overlap integral of the two Doppler-broadened shapes of the incident γ line and the resonance level. It was shown[2] that under certain conditions the value of σ_s, in the V-^{48}Ti scattering process, is strongly dependent on temperature variations of the scatterer and also on its Debye temperature Θ_D. Thus, by comparing the value of σ_s from ^{48}Ti in various chemical forms at two temperatures, $T=295$ K and $T=78$ K, it was possible to obtain the value of Θ_D of ^{48}Ti in $\mathrm{TiH}_{1.85}$, TiO_2, and TiC.

The hydrogenation of Ti was performed in a vacuum glass system utilizing pressures of up to 1 atm. The actual composition obtained was $\mathrm{TiH}_{1.85\pm0.10}$. All the samples were in powder form, each containing ~40 g of Ti, and were sealed in disc-shaped glass containers.

The scattered photons from the targets were detected in a 5 in.×5 in. NaI detector placed at 135° with respect to the photon beam, and the spectrum was analyzed with a multichannel analyzer. In order to obtain a precise determination of the ratios of the scattered intensities, short, 30-min runs were carried out in which the scattered signals from TiC, TiH_2, and TiO_2 were compared with that from pure Ti kept at the same temperature. The results were then normalized to that from Ti whose temperature effect was determined in a separate run. This measurement was repeated several times by using an automatic system which moved the two targets back and forth in and out of the beam, and the two spectra were accumulated in two different memories of the analyzer. In this fashion it was possible to average over long-term drifts of the photomultiplier, the electronic system, the neutron flux of the reactor and possible temperature changes of the vanadium source. Two sets of measurements were carried out, at room temperature and at liquid-nitrogen temperature.

III. THEORETICAL REMARKS

The temperature ratio R is defined as

$$R=\frac{C(78\text{ K},\ 135^\circ)}{C(296\text{ K},\ 135^\circ)}\ , \tag{1}$$

where $C(T,\theta)$ is the scattered intensity at an angle θ (between the scattered and incident directions) at temperature T of the scatterer; $C(T,\theta)$ depends on the nuclear level parameters Γ_0, Γ, δ, and $T_{e,i}$, where Γ_0 is the ground-state radiative width, Γ is the total width, δ is the energy separation between the energies of the incident γ line and the nuclear level of the scatterer, respectively. $T_{e,i}$ is the effective temperature of the scattering atom i (Ti in our case); it can be related to T and to the average energy ϵ_i of the ith atom in a lattice as

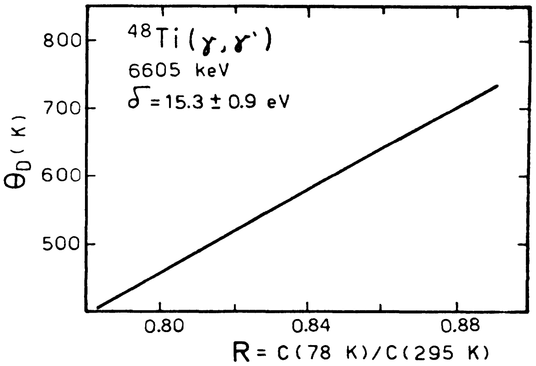

FIG. 1. Debye temperature Θ_D versus the calculated cross-sections ratio R for Ti [see Eqs. (1)—(3)].

$$k_BT_{e,i}\equiv\epsilon_i=\frac{\int_0^\infty S_i(\nu)g(\nu)h\nu\left[\frac{1}{e^{h\nu/k_Bt}-1}+\frac{1}{2}\right]d\nu}{\frac{N_i}{N}\int_0^\infty g(\nu)d\nu}\ , \tag{2}$$

where $S_i(\nu)$ is the fraction of the kinetic energy shared by the ith atom at frequency ν in a molecule such as TiC; N_i is the number of atoms i in a formula unit with N atoms, $g(\nu)$ is the frequency distribution, and k_B is the Boltzmann constant. In case the Debye approximation holds for the ith atom, $T_{e,i}$ may be written as

$$T_{e,i}/T=3\left[\frac{T}{\Theta_D}\right]^3\int_0^{\Theta_D/T}x^3\left[\frac{1}{e^x-1}+\frac{1}{2}\right]dx\ . \tag{3}$$

Equation (3) is the usual Debye approximation for pure elements[14] and it is utilized to obtain the Debye temperature Θ_D of Ti in the various compounds. Θ_D may be related to the maximum frequency $\nu_{m,i}$ of the i atoms by $\Theta_D=h\nu_{m,i}/k_B$. This expression can be used for calculating $T_{e,i}$ and hence the value of R for a given value of Θ_D. The nuclear level parameters necessary for this calculation were reported[13] to be

$$\Gamma_0=0.64\text{ eV},\quad \Gamma=0.86\text{ eV},\quad \delta=15.3\text{ eV}\ .$$

Figure 1 represents the calculated values of R versus Θ_D for Ti. The experimental values of Θ_D for Ti in the various compounds were deduced from the measured values of R and the use of Fig. 1.

IV. RESULTS AND DISCUSSION

A typical scattered photon spectrum from a Ti target as measured by a Ge(Li) detector is given in Fig. 2. It shows, apart from the elastic γ line at 6605 keV, one inelastic line which corresponds to the transition to the first excited state in ^{48}Ti. The integrated intensity of this spectrum in the range $E=5$—6.6 MeV was measured with the

TABLE I. Measured temperature effect R, deduced values of the effective temperature $T_{e,\mathrm{Ti}}$ and the Debye temperature Θ_D in various compounds. For comparison, respective quantities obtained by other experimental techniques are also shown. The absolute errors are given in parentheses.

Compound	R	$T_{e,\mathrm{Ti}}$ (K) Present work 295 K	78 K	$T_{e,\mathrm{Ti}}$ (K) inelastic neutrons 295 K	78 K	Θ_D (K) Present work	Θ_D (K) Low temp. Specific heat
Ti (metal)	0.79 (1)	324 (4)	165 (10)	317[b]	145[b]	420 (30)[a]	420 (Refs. 20)
$TiH_{1.85}$	0.79 (1)	324 (4)	165 (10)			420 (30)	321 (Ref. 26), 293, 268 (Ref. 27)
TiO_2 (rutile)	0.83 (2)	340 (15)	203 (31)			530 (90)	526 (Ref. 21)
TiC	0.86 (2)	361 (12)	242 (22)	354	228	640 (60)	614, 676 (Ref. 19)

[a] The value for Θ_D of Ti from Ref. 20 is used as a "calibration" point for deducing the Θ_D values for the other compounds. It is also utilized to derive $T_{e,\mathrm{Ti}}$ for pure titanium.

[b] These values are calculated from Eq. (2) with $S(\nu)=1$, $N_i=N$, utilizing the Ti phonon frequency spectrum (Ref. 24).

Ti target at two temperatures, $T=78$ K and $T=295$ K. The intensity ratios are given in Table I, together with the values of $T_{e,\mathrm{Ti}}$ and Θ_D extracted from Fig. 1 and Eq. (3). The present results indicate that (1) a significant increase in $T_{e,\mathrm{Ti}}$ and Θ_D was observed in TiO_2 and TiC in comparison with pure metallic Ti, and (2) $T_{e,\mathrm{Ti}}$ and Θ_D are practically unchanged upon hydrogenation of Ti to $TiH_{1.85}$. These results indicate that in TiO_2 and in TiC the Ti atoms are more strongly bonded than in Ti metal. This does not seem to be the case for $TiH_{1.85}$. Although the interpretation of the Ti bond strength in the various compounds seems reasonable, the derived Θ_D and $T_{e,\mathrm{Ti}}$ values should be significant only if the Debye approximation is justified. This is the case if $S_{\mathrm{Ti}}(\nu)g(\nu)$ from Eq. (2) is shown to depend quadratically on the phonon frequency ν. A somewhat weaker but still valid condition may be the requirement that the Ti atoms are predominantly associated with the low-energy (acoustic) phonons while the lighter partners are mainly related to the high-energy (optical) phonons. Information of this kind is best provided by experiments and analysis of inelastic neutron scattering. The most complete and relevant data we were able to obtain, is for TiC. Figure 3(a) exhibits the phonon density of states $g(\nu)$ of TiC (Ref. 15) obtained by model analysis of the phonon dispersion relations in TiC single crystals. The clear separation between low- and high-energy phonons implies a pertinence of the acoustic and optical vibrations to titanium and carbon, respectively. This feature is characteristic also for other transition metal carbides and nitrides[16,17] of the NaCl-type structure for which a single plane may contain a single type of ion. Moreover, the $S_{\mathrm{Ti}}(\nu)$ function [Fig. 3(b)], which does not depend sensitively on the model parameters, definitely demonstrates that the acoustic phonons belong mainly to the titanium atoms. The Debye model may therefore be considered a reliable approximation for Ti in TiC. Furthermore, we used the $g(\nu)$ and $S_{\mathrm{Ti}}(\nu)$ data in Fig. 3 to cal-

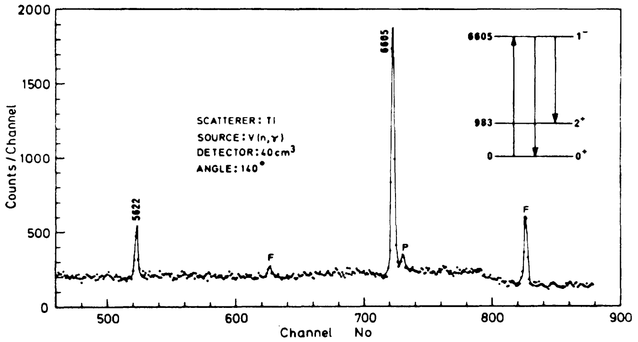

FIG. 2. High-energy part of the γ spectrum from a Ti target at $\theta=140°$ as measured using a 40-cm^3 Ge(Li) detector. The incident γ beam is obtained from the $V(n,\gamma)$ reaction. The corresponding decay scheme to the ground and first excited state in ^{48}Ti is also shown. P and F refer to photo- and first-escape peaks; other energies refer to double-escape peaks.

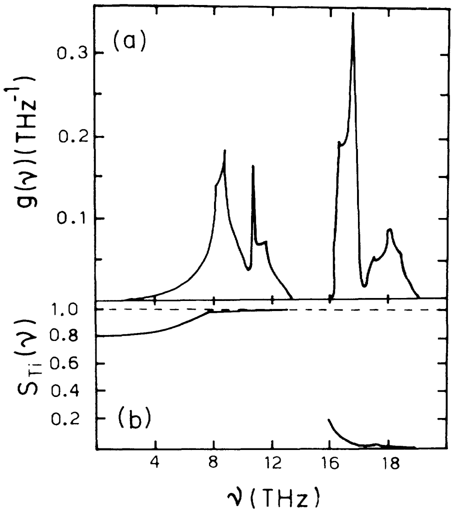

FIG. 3. (a) Shell-model calculation of the phonon density of states in TiC at room temperature (Ref. 15). (b) Shell model calculation of the $S_{\mathrm{Ti}}(\nu)$ function in TiC [Pintschovius (private communication). The curve was calculated from the 12-parameter shell model described in Ref. 15].

culate $T_{e,\mathrm{Ti}}$ (295 K) for TiC, and obtained

$$T_{e,\mathrm{Ti}}(295\ \mathrm{K})=354\ \mathrm{K}$$

in very good agreement with our experimental value of 361 ± 12 K obtained from Eqs. (1) and (3) and Fig. 1. This agreement shows that our results are entirely consistent with neutron scattering measurements, as was also shown for metallic Ni and Pb (Ref. 18).

Since the Ti atoms in TiC take part mainly in the acoustic part of the vibrational spectrum (Fig. 3), it is of interest to compare the Θ_D values from the present measurement with those obtained from low-temperature heat capacity or elastic measurements (Table I). It should be stressed that the Debye temperatures cited hereafter from other works are either originally derived or normalized according to the convention that only Ti atoms contribute to the low-temperature Θ_D values. As we mentioned before, this is indeed the case for TiC. However, it is not clear whether this assumption is valid for TiO_2 and $TiH_{1.85}$.

The Θ_D values determined for TiC ($\Theta_D=614$ and 676 K) (Ref. 19) by low-temperature C_p measurements are in a good agreement with the value derived in the present work ($\Theta_D=640\pm60$ K). A Debye temperature about 10—15 % higher has been reported from elastic constant measurements.[19] A good agreement exists also in the case of TiO_2, for which $\Theta_D=526$ K has been reported from low-temperature heat capacity measurements.[21] This value should be compared to the presently derived $\Theta_D=530\pm90$ K and to $\Theta_D=503$ K, 494 K (Ref. 22) from elastic constant measurements. The phonon density of states in TiO_2 (Ref. 23) does not indicate any distinct separation between acoustic and optical vibrations as is observed in TiC. Unfortunately we do not have information on the $S_{\mathrm{Ti}}(\nu)$ function of TiO_2. Such information might enable a more decisive conclusion about the validity of the Debye approximation for Ti in TiO_2.

The inelastic neutron scattering spectrum of polycrystalline $TiH_{1.92}$ (Ref. 25) does indicate a separation between acoustic and optical phonons. However, the relative weight of the low-energy part of the spectrum is significantly smaller from what might be expected if one third of the atoms (the titanium atoms) contribute to it. Two Θ_D values have been reported for TiH_x from low-temperature heat-capacity experiments: Ducastelle *et al.*[26] have obtained Θ_D ($TiH_{1.75}$)$=321$ K and Bohmhammel *et al.*[27] have reported Θ_D ($TiH_{1.76}$)$=293$ K, Θ_D ($TiH_{1.85}$)$=268.2$ K. The latter two values have been derived by using two Debye functions. Our result (420 ± 30 K) differs significantly from the above data. This discrepancy may be accounted for by two possible reasons: Firstly, the Debye model may not be a good approximation for Ti in TiH_2. The second reason is associated with the existence of the Jahn-Teller (JT) effect in TiH_x, e.g., (Refs. 26 and 28). This effect is temperature dependent and causes a fcc-fct distortion for $x\geq1.7$ below a transition temperature $T_{\mathrm{JT}}\simeq310$ K. A pronounced temperature dependence of Θ_D may be induced in the vicinity of the Jahn-Teller transition, while in using Eqs. (1) and (3) we have assumed a constant Θ_D at 80 and 295 K. It has been also suggested[6] that the Jahn-Teller effect causes the relatively low Θ_D values in TiH_x.

In summary we have derived the effective and the Debye temperatures of Ti in the interstitial compounds $TiH_{1.85}$, TiO_2, and TiC. A comparison of our results with those from other experimental techniques supports the applicability of the Debye model to Ti in TiC and probably in TiO_2. The present data imply that the Debye approximation is not valid for Ti in $TiH_{1.85}$ although it exhibits the largest mass ratio of its two components among the three compounds studied in this work. Such an inference cannot be regarded, however, as a definite one mainly because of the "complication" introduced into TiH_x by the Jahn-Teller-induced tetragonal distortion near room temperature. An interesting hypothetical possibility might be a significant Ti contribution to the optical-phonon region in resemblance of the hydrogen contribution to the low energy host phonons in some hydrides.[7–9]

Finally, it should be mentioned that a model-independent determination of the energy ϵ_i defined in Eq. (2), from nuclear γ resonant scattering experiments is possible[18] and may be of importance for shedding more light on the bonding strength of various compounds. Our present efforts are concentrated in this direction.

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