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Temperature dependence of the elastic shear modulus of the Laves-phase materials TaV_2 and TaV_2H_x

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Abstract

Resonant ultrasound spectroscopy has been used to measure the shear modulus of polycrystalline TaV_2H_x for $x = 0$, 0.06, 0.10, 0.18, 0.34, and 0.53 over the temperature range of 20–300 K. The results show a strong influence of hydrogen on both the magnitude and the temperature dependence of the shear modulus of these materials. These results are in qualitative agreement with a model involving the electronic structure of these C15 Laves-phase materials. The symmetry of the C15 structure results in doubly-degenerate electronic energy levels at the X point of the Brillouin zone. These levels couple to the shear strain e_4 with resulting effects on the single-crystal elastic constant c_{44}. The strong temperature and concentration dependence of c_{44} contributes to the measured shear moduli of these polycrystalline materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The second-order elastic constants of materials are given by the second derivative of a thermodynamic potential with respect to strain. For adiabatic elastic constants the appropriate potential is the internal energy while for isothermal elastic constants it is the Helmholtz free energy [1,2]. The anharmonic nature of lattice vibrations leads to a dependence of the elastic constants on the temperature, T. In metals there is also a contribution from the conduction electrons. The lattice vibrations result in a T^4 term at low temperatures and a term linear in temperature at high temperatures [3]. For simple metals the electrons contribute a T^2 term at low temperatures [4]. The overall result is that the elastic moduli approach 0 K with zero slope, but decrease monotonically with increasing temperature. The picture is not as simple for materials undergoing phase transitions [5,6] or for materials with a more complicated electronic structure [7].

The elastic moduli of a number of Laves-phase compounds have been found to have an unusual dependence on temperature. Chu et al. [8] found that the shear modulus (G) and Young's modulus (E) in $Hf_{25}V_{60}Nb_{15}$ increased with increasing temperature (70–300 K) while the bulk modulus (B) was virtually temperature independent. Takashima and Hayashi [9] (1973) found anomalous behavior of the longitudinal wave sound velocities in polycrystalline HfV_2 and ZrV_2. The velocities decreased on cooling from room temperature to 115 K, then increased with further cooling. Polycrystalline TaV_2, however, showed only a slight increase of the longitudinal velocity on cooling from room temperature to 4.2 K [9]. Balankin et al. [10,11] measured the temperature dependence of G and E in HfV_2 and ZrV_2. Both compounds showed a V-shaped minimum in $G(T)$ centered at temperatures of ≈ 110 K and an anomalous increase with increasing temperature above 110 K up to the vicinity of the melting temperature (≈ 1500 K).

We have recently measured [12] the elastic moduli of TaV_2 down to low temperatures. Both G and E showed an anomalous temperature dependence. These moduli increase with increasing temperature over the entire temperature range of 4–345 K. Remarkably, the addition of relatively small amounts of hydrogen or deuterium completely changes this temperature dependence. Both G and E of $TaV_2H_{0.34}$, $TaV_2H_{0.53}$, and $TaV_2D_{0.17}$ decrease with increasing temperature. The anomalous elastic properties of the C15 Laves-phase materials have been attributed to an electronic band-structure effect [13–16]. The symmetry of the C15 lattice allows for a double degeneracy of the electronic energy levels at the X-point of the Brillouin zone with a linear dispersion in the vicinity of this point. If

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the Fermi level lies near the double-degeneracy point, strong effects on the elastic constant may result. The effects are quite sensitive to the distance of the Fermi level from the double-degeneracy point. For the C15 structure, these electronic energy levels couple to a type e_4 strain resulting in changes in the single-crystal elastic constant c_{44}. In Ref. [12] it was proposed that the addition of hydrogen raises the Fermi level (by means of the electrons contributed), and thus changes the influence of these special electronic energy levels on c_{44}. Laves-phase materials are of increasing interest for high-temperature structural applications [17]. In addition, many of these intermetallic compounds store appreciable amounts of hydrogen. Thus, it seems important to explore in more detail this unusual influence of hydrogen on the elastic moduli of TaV_2. The present paper presents results for the temperature dependence of the elastic moduli of TaV_2H_x for a range of x. The results are interpreted in terms of the electronic band-structure.

2. Experimental details

The polycrystalline TaV_2 samples were prepared by arc melting mixtures of the appropriate amounts of the high-purity constituent elements in an argon atmosphere followed by various annealing procedures [18]. Samples of TaV_2H_x were prepared as described previously [18].

Ultrasonic measurements were made on samples of TaV_2H_x for $x=0$, 0.06, 0.10, 0.18, 0.34, and 0.53. A low-speed diamond saw was used to cut the samples into approximate rectangular parallelepipeds (RPs) from the button ingots. These saw-cut pieces were then hand-polished into accurate RPs with edge dimensions in the order of 1–2 mm. The technique of resonant ultrasound spectroscopy (RUS) was used to measure the adiabatic polycrystalline elastic moduli [19–22]. With RUS, a large number of the lowest natural mechanical resonances of the RP samples are excited and their frequencies measured. The swept-sine measurements were made using a commercial spectrometer (Dynamic Resonance Systems). The elastic constants were determined by performing an iterative computation which minimizes the error between the measured and computed frequencies [20]. In all cases, the frequencies of 40–50 resonances were measured with the typical rms difference between the measured and computed frequencies being between 0.25 and 0.40%. For materials with isotropic symmetry only two independent moduli are required to fully define the elasticity of the system. The polycrystalline elastic moduli C_{11} and C_{44} were derived directly from the measured frequencies. C_{44} is just the usual polycrystalline shear modulus G [12].

The mass density is needed to determine the elastic moduli from the measured frequencies. The room-temperature densities (ρ_M) as determined by direct measurement of the mass and sample dimensions were used. Taking into account the rms errors in the fit as well as errors in sample dimensions and density measurements, the resulting overall error in the absolute value of G is estimated to be 1%. The relative error is, of course, much smaller and is essentially indicated by the scatter in the data.

Theoretical densities (ρ_T) were calculated from the experimentally-determined room-temperature lattice parameters [23]. The measured densities are about 4% lower than the theoretical densities. It is not surprising that the measured densities may be somewhat lower than those calculated from the X-ray lattice parameters due to the presence of grain boundaries, dislocations and possible microvoids in the polycrystalline materials. The differences between the two sets of densities, while reasonable, could have some effect on the absolute value of the measured elastic moduli. The measured densities, not the theoretical densities, were used in the computation of the elastic moduli from the measured frequencies. In any case, the main focus of the present study is on the temperature dependence of the moduli. Because thermal expansion data are not available for these materials the results have not been corrected for thermal contraction; the room temperature dimensions and density have been used in the analysis. It is expected that this neglect will lead to a small error [12]; that is, the total increase in the elastic constants as the temperature is lowered from room temperature to 4 K is expected to be about 0.15–0.20% greater than the values reported below.

3. Results and discussion

Fig. 1 gives results for the shear modulus for polycrystalline TaV_2H_x for $x=0$, 0.06, 0.10, 0.18, 0.34, and 0.53. Fig. 1 illustrates the anomalous temperature dependence of G for TaV_2 previously reported [12]; the shear modulus increases with increasing temperature throughout the range of 25–300 K. The modulus for $TaV_2H_{0.06}$ shows a qualitatively similar, but weaker, temperature dependence. The modulus for $TaV_2H_{0.10}$ goes through a shallow minimum near 40 K. This minimum is just barely visible in Fig. 2 where the results for these three materials are shown on an expanded scale. As Fig. 1 shows, the temperature dependence is reversed for the higher hydrogen concentrations. In addition to its effect on the temperature dependence of the shear modulus, hydrogen has a strong influence on the magnitude of the modulus; at 25 K the shear modulus of $TaV_2H_{0.53}$ is 55% greater than that of TaV_2.

The modulus shift apparent for the higher hydrogen concentrations in the temperature range of 225–300 K is associated with the hydrogen motion [24]. The present measurements were made in a frequency range of 0.5–2 MHz. The condition $\omega\tau\approx 1$ is satisfied at about 260 K where ω is the angular frequency of the ultrasound and τ is the hydrogen hopping time. At temperatures below

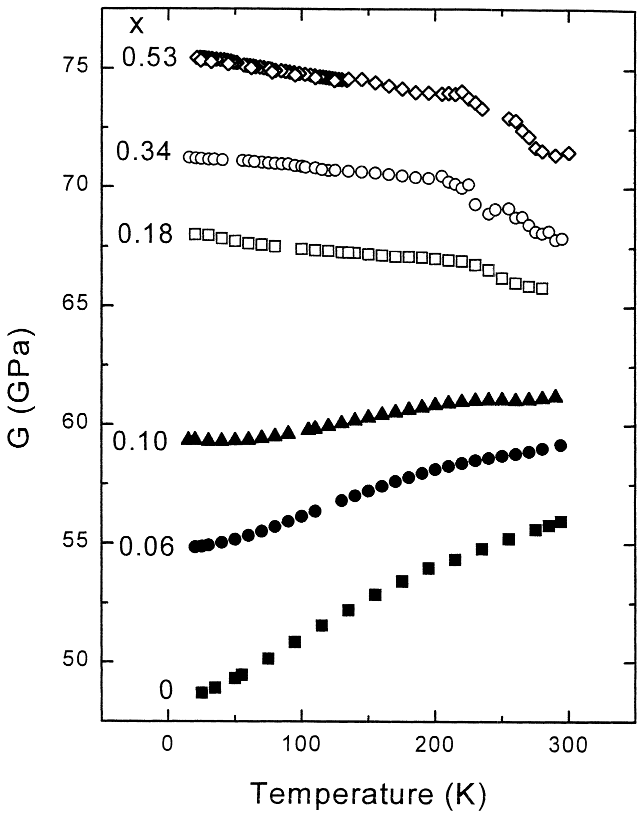

Fig. 1. Temperature dependence of the shear modulus of polycrystalline TaV_2H_x for $x=0$, 0.06, 0.10, 0.18, 0.34 and 0.53.

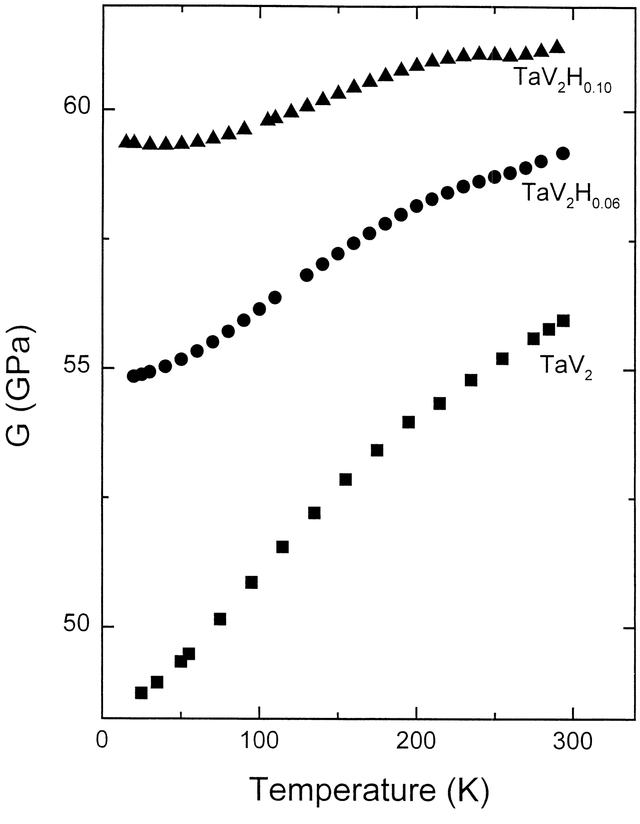

Fig. 2. An expanded view of the data of Fig. 1 for $x=0$, 0.06, and 0.10.

about 225 K the results represent the unrelaxed modulus [25], while the relaxed modulus is observed at temperatures above about 300 K. A more detailed account of the modulus change due to the hydrogen motion will be presented in a future publication and will not be discussed further in the present article.

We interpret the results in terms of the unusual electronic structure proposed for the *C*15 materials [13–16]. The C15 symmetry allows for doubly-degenerate electronic energy levels at the *X*-point of the Brillouin zone with a linear dispersion in the vicinity of this point. The degeneracy and linear dispersion were confirmed by a band-structure calculation [15,16]. By symmetry these levels couple to a strain e_4 [13]. If the Fermi level is near the double-degeneracy point, then a strong contribution to the temperature dependence of the corresponding elastic constant c_{44} may result. The Helmholtz free energy of a system of N electrons each of energy ξ_{bk} is given by

$$F = N\xi_F - 2\sum_{bk} k_B T \ln\left[1 + \exp\frac{\xi_F - \xi_{bk}}{k_B T}\right] \tag{1}$$

where ξ_F is the Fermi energy, the sum is over all energy bands b and all k values, and the factor 2 accounts for spin. We consider only the doubly-degenerate levels in the vicinity of the X point and express these levels as [13]

$$\xi_{1,2}(k_z) = \pm\sqrt{(sk_z) + (De_4)^2} \tag{2}$$

where ξ_F, $\xi_{1,2}$, and k are measured with respect to the doubly degenerate point, s is a proportionality constant, and D is a constant representing the electron-phonon coupling.

Using $c^e_{44} = \delta F^2/\delta e_4^2$ gives in the present case the simple result

$$c^e_{44} = \pm 2D^2 \sum_k \frac{f(k_z)}{sk_z} \tag{3}$$

where $f(k_z)$ is the Fermi–Dirac distribution function. Setting $\epsilon = sk_z$ and converting the sum to an integral results in [12]

$$c^e_{44}\alpha - D^2 \int_0^{\Omega} \frac{d\epsilon}{\epsilon}\left[\frac{\sinh(\epsilon/k_B T)}{\cosh(\epsilon/k_B T) + \cosh(\xi_F/k_B T)}\right] \tag{4}$$

where the qualitative features are not strongly dependent on the range of integration, Ω. The band-structure calculation [15,16] indicates that $\Omega = 5000$ K represents a reasonable range for the linear dispersion, and this value will be used below. Fig. 3 gives the results from Eq. (4) for various values of the Fermi energy. Comparing Figs. 1 and 2 with Fig. 3 shows that this simple model for electronic effects accounts for the major features of the shear modulus data. The comparison of experimental results with the model indicates that the Fermi level for TaV_2 lies very near the double-degeneracy level at the X point. The band-structure calculation [15,16] indicated that the Fermi level is 6.0 mRyd (1000 K) above this level. Our

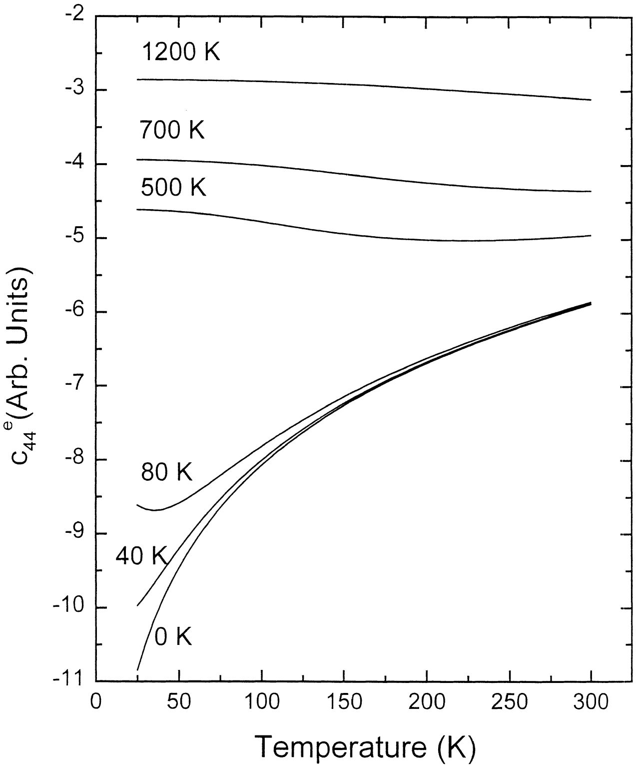

Fig. 3. Theoretical curves showing the electronic contributions predicted by Eq. (4) for various values of the Fermi energy. The units of C_{44}^{e} are arbitrary.

results are in disagreement with this value. For measurement temperatures down to 20 K, no minimum is observed for the shear modulus of TaV_2 and $TaV_2H_{0.06}$. This indicates that the Fermi level for these materials is less than 40 K above the double-degeneracy level. A shallow minimum is found for $TaV_2H_{0.10}$ at about 40 K which indicates that the Fermi level for this material is about 80 K above the double-degeneracy level. For the higher concentration materials, $x \geq 0.17$, no minima are found up to 300 K which suggests that the Fermi level for these materials is more that 600 K above the double-degeneracy level. The Fermi levels indicated in Fig. 3 are for illustrative purposes only, and are not meant to be a fit to the data. We refrain from a more detailed attempt to fit our experimental results to Eq. (4) for several reasons. The theoretical result only includes an electronic contribution to the single-crystal elastic constant c_{44}. There will be other contributions to c_{44} due to the usual lattice anharmonicity. In addition, our measurements are on polycrystals with the result that the measured shear modulus has contributions from the single-crystal elastic constant in addition to c_{44}.

4. Summary

Ultrasonic measurements on polycrystalline TaV_2H_x for various values of x ranging from 0 to 0.53 show a strong influence of hydrogen on both the magnitude and the temperature dependence of the shear modulus over the temperature range of 20–300 K.

These results are in qualitative agreement with a model involving electronic contributions to the single-crystal elastic constant c_{44}. The symmetry of the C15 structure results in doubly-degenerate electronic energy levels at the *X* point of the Brillouin zone. These levels couple to the shear strain e_4 with resulting contributions to the elastic constant c_{44} which in turn affects the measured moduli of the polycrystalline samples. Measurements at both higher and lower temperatures are needed to further explore the implications of the theoretical model. Such measurements are under way.

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