

Elastic moduli of a Ti-Zr-Ni icosahedral quasicrystal and a 1/1 bcc crystal approximant

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Resonant ultrasound spectroscopy has been used for the measurement of the elastic moduli of a Ti-based quasicrystal, one of the major classes of quasicrystals. Both the bulk and shear elastic moduli of a Ti-Zr-Ni multigrained icosahedral quasicrystal and a polycrystalline 1/1 approximant were measured over the temperature range of 15–300 K. The elastic moduli of these two materials are very nearly the same, a result in agreement with the belief that the structures of these two materials are closely related. The temperature dependence of the moduli resembles that of ordinary metals. The results have been used to predict the acoustic contribution to the low-temperature specific heat. This contribution is much larger in these Ti-based materials than for the Al-based quasicrystals reported by others. Besides their general interest, the elastic moduli are useful for constructing atomic potentials in these unusual materials. [S0163-1829(99)09517-X]

I. INTRODUCTION

Since the discovery¹ of intermetallic alloys with long-range aperiodic order and crystallographically forbidden rotational symmetries, a large body of theoretical and experimental work has been devoted to the study of these novel materials, known as quasicrystals.² Most of the studies have dealt with the Al-based quasicrystals. This class of materials was the first to be discovered and several phases are known to be stable. Several elastic modulus studies have been performed on the Al-based quasicrystals. These experiments showed,^{3–6} with increasing precision, that the icosahedral phase quasicrystals exhibit the theoretically expected⁷ elastic isotropy. A more recent experiment⁸ showed that the decagonal Al-Ni-Co quasicrystal is, as expected, transversely elastically isotropic.

While the largest class of quasicrystals is the aluminum-based one, the second largest class is based on titanium.⁹ Recently, a stable Ti-Zr-Ni quasicrystal has been discovered.^{10,11} In addition, a closely related 1/1 crystal approximant to the stable Ti-Zr-Ni quasicrystal has been found.^{12,13} These Ti-based materials can absorb and desorb considerable amounts of hydrogen¹⁰ making them of potential use for hydrogen storage. There appear to have been no studies of the elastic properties of the Ti-based materials. Elastic constants are of fundamental importance. Ultrasonic measurements yield the adiabatic moduli and thus are the second derivative of the internal energy with respect to the strain. They are directly related to the atomic bonding strength and are often used as a test of first-principles total-energy calculations. The lack of periodicity in quasicrystals makes the determination of their atomic structure difficult. To be viable, structures proposed from diffraction and electron microscopy studies should be stable to small fluctuations. Measured elastic constants are critical for refining the shape of the atomic potentials used in these studies. In addition, elastic constants are related to thermal properties through the Debye theory. In particular, elastic constant mea-

surements can be used to calculate the low-temperature acoustic contribution to the specific heat¹⁴ which has a characteristic T^3 temperature dependence. In the case of Al-Mn-Pd and Al-Re-Pd icosahedral quasicrystals, the measured low-temperature T^3 specific heat was larger than that expected from the sound velocity measurements, revealing an excess specific heat of uncertain origin. Apparently there have been, as yet, no measurements of the low-temperature specific heat in the Ti-based quasicrystals.

Given the importance of the elastic moduli, the lack of data for this class of materials, and the availability of relatively large stable specimens, we undertook elastic constant measurements on both the Ti-Zr-Ni quasicrystal and its 1/1 crystal approximant. The results are reported here.

II. SAMPLES AND EXPERIMENTAL DETAILS

Alloys of the desired composition, $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ for the i phase and $\text{Ti}_{44}\text{Zr}_{40}\text{Ni}_{16}$ for the 1/1 approximant phase, were prepared by arc-melting mixtures of the pure elements on a water-cooled copper hearth in a high-purity Ar gas. The i phase quasicrystal and W phase approximate were prepared by annealing the resulting ingots in a graphite crucible, which was placed inside a quartz tube. A Ti-Zr alloy, used as an oxygen getter, was also placed in the tube, but was separated from the sample. The tube was then evacuated and sealed under a vacuum of 10^{-5} – 10^{-6} torr. Oxygen contamination of the sample during annealing was prevented by first heating the Ti-Zr getter to 1000 °C for 10 min by rf induction, while keeping the alloy ingot in the graphite crucible at room temperature. The tube containing the sample and the getter was then annealed in a furnace for the required time: 610 °C for 64 h to obtain the W phase and 570 °C for 64 h to form the i phase. Phase purity was confirmed by x-ray and transmission electron microscopy (TEM) investigations. TEM microstructural studies of both samples revealed a distribution of grain sizes, with a largest diameter of a few μm .

Samples in the approximate shape of rectangular parallel-

epipeds, about 1–2 mm on an edge, were cut from the ingots using a low-speed diamond saw. These saw-cut pieces were then polished into rectangular parallelepipeds for the ultrasonic measurements with room temperature dimensions of $1.321 \times 1.100 \times 1.644 \text{ mm}^3$ for the *i*-phase material and $2.197 \times 1.318 \times 1.621 \text{ mm}^3$ for the *W*-phase material. The room-temperature densities, determined by immersion weighing in toluene, were found to be $6.081 \pm 0.008 \text{ g/cm}^3$ for the *i*-phase material and $6.066 \pm 0.01 \text{ g/cm}^3$ for the *W*-phase material. The elastic constant measurements were made using the technique of resonant ultrasound spectroscopy (RUS).^{15–18} This experimental technique permits accurate elastic constant measurements on the millimeter-sized samples available for the present study. With this technique a sample is placed corner to corner between two piezoelectric transducers one of which is used for excitation and one for detection. By sweeping the excitation frequency, a large number of the lowest frequency vibrational eigenmodes of the parallelepiped can be measured. The elastic constants were determined from the measured frequencies by an iterative computation which minimizes the error between measured and computed frequencies.¹⁹ We measured the first 50 frequencies for each specimen with a typical rms difference between measured and computed frequencies of 0.15–0.20%. The measurements were carried out over the temperature range of 15–300 K. The temperature was controlled using an electronic controller with heater and a gas flow cryostat. A calibrated silicon diode was used for temperature measurements.

III. RESULTS AND DISCUSSION

We analyze our measurements in terms of two independent elastic constants as appropriate for isotropic materials. As mentioned in the previous section, the typical grain size of the materials studied is much smaller than the sample size. There is no reason to assume any preferred orientation (texture) for these grains, thus we assume elastic isotropy in the analysis. This argument applies for both the *i*-phase and the *W*-phase materials. It is expected that the *i*-phase material would be elastically isotropic^{6,7} even if measurements could be made on a single grain. We fit our measured frequencies to the elastic constants C_{11} and C_{44} where the subscripts refer to a coordinate system aligned with the sample parallelepiped axis. We present the results, however, in terms of the shear modulus G and the bulk modulus B , where

$$G = C_{44} \quad \text{and} \quad B = C_{11} - \frac{4}{3}C_{44}. \quad (1)$$

To the extent that the *i*-phase material is intrinsically isotropic, G and B represent the two independent elastic constants for this material. For the *W*-phase material, G and B represent the usual polygrained averages. Figure 1 presents results for the shear modulus G over the temperature range of 15–300 K for the *i*-phase quasicrystal and the *W*-phase crystal approximate. Figure 2 presents similar results for the bulk modulus B . The overall temperature dependence of the moduli is similar for the two materials, although there is a small difference. The *W* phase shows a slightly stronger increase in the moduli with decreasing temperature and is, in some sense, more anharmonic. We estimate the absolute accuracy of the measurements, based on the quality of the fit

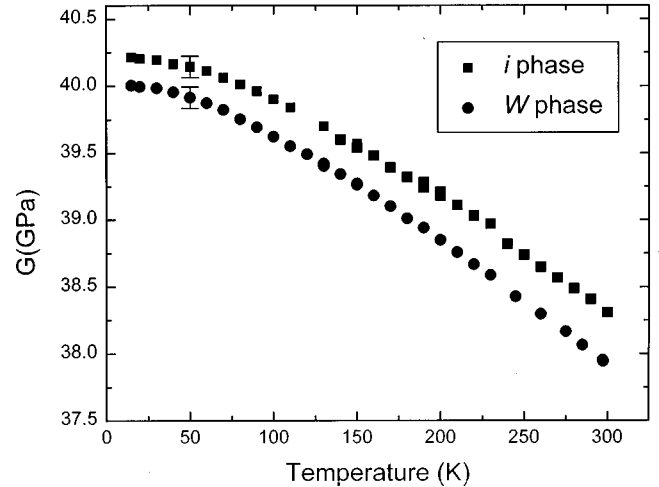


FIG. 1. Shear modulus G vs temperature for a Ti-Zr-Ni quasicrystal (*i* phase) and a 1/1 crystal approximant (*W* phase). Typical error bars for the absolute accuracy are shown.

and errors in density measurement, to be 0.2% for G and 2% for B . The accuracy is higher for G than for B because many of the lower frequency resonances depend strongly on G , but that is not the case for B . From Figs. 1 and 2 it can be seen that the absolute error in the modulus measurements is considerably larger than any random scatter in the data presented. This is because the contributions to the total absolute error from the density and the quality of the RUS fit are systematic across the temperature range studied.

Because thermal expansion data are not available for these materials at low temperatures the results have not been corrected for thermal contraction; the room-temperature dimensions and density have been used in the analysis. Taking into account the direct dimensional effects as well as the indirect effect through the density, the elastic constants deduced from the measured frequencies vary inversely as the dimension. Metals such as Ti have a total thermal contraction between room temperature and 4 K of about 0.15–0.20%.²⁰ Assuming that the materials in the present

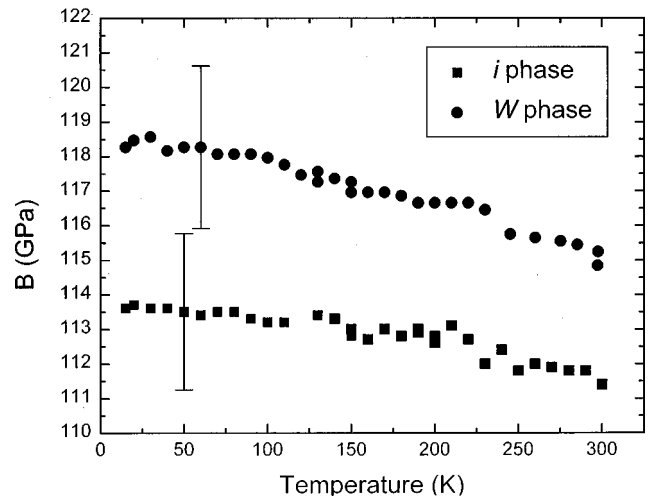


FIG. 2. Bulk modulus B vs temperature for a Ti-Zr-Ni quasicrystal (*i* phase) and a 1/1 crystal approximant (*W* phase). Typical error bars for the absolute accuracy are shown.

study behave similarly, the neglect of thermal contraction effects in the analysis of the data leads to a comparable error; that is, the total increase in the elastic constants as the temperature is lowered from room temperature to 15 K would be about 0.15–0.20% greater than shown in Figs. 1 and 2.

A comparison was made of the values of G and B obtained in the present experiment with literature values for those of the constituent metals Ti, Zr, and Ni.²¹ For a crude comparison a weighted average for $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ (i -phase composition) was calculated. In this way values of 115.7 and 117.9 GPa were estimated for B at room temperature and 4 K, respectively. Remarkably, these values are almost the same as those measured for the i - and W -phase materials. For G , the computed aggregate value depends on the method of averaging the single-crystal values. We used the mean of the Voigt and Reuss averages for the hexagonal metals titanium and zirconium. (The Voigt and Reuss averages differ by only a few percent in these cases.) For the cubic material nickel we used the Kröner average.²² The corresponding calculated values for G are 47.7 and 54.2 GPa, some 35% higher at low temperature than those measured for the i and W phases. These results imply that for hydrostatic compression both phases of this material appear to behave approximately as the weighted average of the constituent materials, but they are softer in shear than the weighted average of the constituent materials.

The present measurements can be used to compute the long-wavelength phonon contribution to the heat capacity C_{ac} . In the low-temperature limit the specific heat is given by²³

$$C_{ac} = \frac{2\pi^2 k_B^4}{5\hbar^3 \nu_0^3} T^3, \quad (2)$$

where ν_0 is an average sound velocity which in the present case is given by

$$\frac{1}{\nu_0^3} = \frac{1}{3} \left(\frac{1}{\nu_l^3} + \frac{2}{\nu_t^3} \right), \quad (3)$$

where the subscripts l and t refer to the longitudinal and transverse sound velocities, respectively. Using the results reported above it is found that $\nu_0 = 2.89 \times 10^3 \pm 10$ m/s for both the i - and W -phase materials. The acoustic contribution to the low-temperature molar specific heat is found to be $C_{ac}/T^3 = 5.64 \times 10^{-5} \pm 0.05 \times 10^{-5}$ J/(mol K⁴) for the i phase, and $5.59 \times 10^{-5} \pm 0.05 \times 10^{-5}$ J/(mol K⁴) for the W phase. These values are considerably larger than the predicted acoustic contribution in decagonal Al-Ni-Co [0.893×10^{-5} J/(mol K⁴)],^{8,24} or icosahedral Al-Mn-Pd [1.63×10^{-5} J/(mol K⁴)].¹⁴ The reason for the difference is the lower ν_0 in Ti-Zr-Ni as compared to the other materials.

IV. CONCLUSIONS

We have measured the shear modulus G and the bulk modulus B of icosahedral Ti-Zr-Ni (i phase) and a Ti-Zr-Ni crystal approximate (W phase). Assuming that the i -phase material is intrinsically isotropic as is expected theoretically and experimentally for this symmetry, G and B represent the two independent elastic constants for this material. For the W -phase material, G and B represent polygrained averages. The elastic moduli of these two materials are very nearly the same. This result provides further evidence for the close similarity of this quasicrystal and its 1/1 crystalline approximant. The temperature dependence of the moduli resembles that of ordinary metals. The moduli for the W phase are slightly more temperature dependent than those for the i phase. The results allow us to estimate the acoustic phonon contribution to the low-temperature specific heat which is considerably larger for the Ti-based materials than for the Al-based materials reported by others. These results should prove useful in the construction of atomic potentials for these materials.

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