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Young's Modulus and Internal Friction of Yttrium

A.M. Tishin, S.A. Nikitin and V.Yu Bodriakov

Physics Department of Moscow State University, Moscow, 119899, Russia

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Abstract. — A detailed study of the temperature dependence of Young's modulus $E(T)$ and internal friction $Q^{-1}(T)$ has been made for various purity single crystals and polycrystalline samples of yttrium. Measurements have been carried out in the temperature range $4.2 - 400$ K at frequencies $f \sim 1$ kHz. It was found that $E_{\text{ep}} = 134$ GPa and $E_c = 51$ GPa at $T = 4.2$ K in the basal plane and along the c-axis, respectively. It was established that the $E(T)$ curves for single crystals have a Debye-like shape in the temperature interval $4.2 - 320$ K (the Debye temperature $\Theta_D = 135$ K and $\Theta_D = 98$ K in the case of basal plane and the c-axis, respectively. $Q^{-1}(T)$ at a temperature near $400$ K displays maxima connected with relaxation processes of defects and dislocations in the samples.

1. Introduction

The study of elastic and inelastic characteristics of various metals is very important from both the scientific and the technical points of view. Such investigations of high purity samples are of special interest owing to the essential effect of purity and preparation techniques on the properties above.

In this work, a detailed study of Young's modulus $E$ and internal friction $Q^{-1}$ has been carried out with various purity samples of yttrium. This material attracts the attention of investigators for a number of reasons. The yttrium ion possesses an external electronic shell $4d^{1}5s^{2}$ which is the same as the shells of heavy rare earth metals (REM), and it is also trivalent. Being a Pauli paramagnet, yttrium has a hexagonal closed packed structure and REM-like Fermi surface [1,2]. The state diagrams of yttrium with scandium and other rare earth metals are characterized by continuous rows of solid solutions of isomorphous modifications (except for Y-La and Y-Ce systems). So, yttrium in alloys with heavy REM plays the part of an ideal magnetic solvent which increases the distance between the rare earth ions.

The main physical properties of yttrium are now well enough studied. The heat capacity was studied in references [3–5], the heat expansion in reference [6]. The Hall effect [7] and defects of crystalline lattice [8] were also investigated. The anisotropic crystalline lattice of yttrium gives rise to essential differences of physical properties of the metal along various crystallographic directions. For example, electrical resistivity observations [9,10] of Y single crystals showed

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that, near room temperature, the resistivity $\rho_{300}^b$ measured along the $b$-axis exceeds by a factor of two the value $\rho_{300}^c$ measured along the $c$-axis: $(\rho_{300}^b - \rho_{300}^c)/(\rho_{300}^c - \rho_{4.2}^c) = 2.0$. This fact is explained by the essential anisotropy of the Fermi surface of yttrium, whose cross sections along the $c$- and $b$-axes differ from each other by a factor of two [9]. The values of the Debye temperature of the metal, $\Theta_D$, defined from measurements of heat capacity [3–5,11], electrical resistivity [9], neutron diffraction [12], etc., considerably differ from each other and vary from $\Theta_D = 187.5$ K [10] up to $\Theta_D = 330$ K [13]. However, most values reported lie between 232 and 258 K.

Experimental and theoretical works [14–18] have been devoted to the study of the elastic properties and internal friction in yttrium. A detailed investigation of the elastic constants $c_{ij}$ was carried out for $Y$ single crystal [14]. In this article, the calculations give the value averaged along different crystallographic directions of Young’s modulus $E = 63.6$ GPa at room temperature. It has been observed [17] that the modulus changes from 68.6 GPa along the $c$-axis to 65.0 GPa along the $a$-axis. The theoretical calculations [18] of the elastic constants of yttrium are in a reasonable agreement with experimental data [14]. Results of the study of the dynamic modulus $G$ and internal friction $Q^{-1}$ have been reported in references [15, 16] for the temperatures from 78 to 300 K. Internal friction was found to be strongly dependent on the heat treatment and purity of samples [18]. Thus the investigations of Young’s modulus $E$ and internal friction $Q^{-1}$ carried out on various purity yttrium in a wide temperature region and the determination of the Debye temperature for samples with low impurity content are of doubtless interest.

For the reasons mentioned above single crystals of $Y$ along the $c$-axis (sample C) and in the basal plane (sample B), and textured polycrystalline (with main direction of texture along the $a$-axis purified yttrium (sample T) have been studied at temperatures from 4.2 to 400 K. Such extensive investigations of yttrium at sound frequencies had not been carried out yet [19].

2. Experimental Details

A single crystal of yttrium was obtained by potless zone melting with inductive heating in helium atmosphere. The content of the main metallic impurities in this yttrium after vacuum distillation was determined by chemical and atomic-absorption analysis. The results are presented in Table I. Annealing of the crystal was done in a vacuum of about $10^{-6}$ torr at 800°C during 10 hours. The single crystal was oriented by the conventional back Laue reflection method with an accuracy of $\pm 3^\circ$. Purified yttrium was obtained by the vacuum distillation method with condensation of vapors in solid state on a copper water-cooled backing. Purification was made in a resistance furnace with a graphite heater at a remaining pressure of about $5 \times 10^{-8}$ torr. As a result of a sublimation process of 10 hours, textured ingots of densely

### Table I. — Impurities content in single crystal yttrium.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Content, wt%</th>
<th>Impurity</th>
<th>Content, at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.009</td>
<td>Cu</td>
<td>0.022</td>
</tr>
<tr>
<td>N</td>
<td>0.0015</td>
<td>Mg</td>
<td>0.001</td>
</tr>
<tr>
<td>C</td>
<td>0.011</td>
<td>Al</td>
<td>0.005</td>
</tr>
<tr>
<td>Impurity</td>
<td>Content, at%</td>
<td>Dy</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.001</td>
<td>Ca</td>
<td>0.001</td>
</tr>
</tbody>
</table>
joined crystallites of yttrium with cross sections of $2 \times 2 \text{ mm}^2$ and up to 15 mm long were obtained [20]. The crystallites were oriented along one of the three principal crystallographic directions [1124], [1120] or [1010]. The purest yttrium was obtained after additional cycles of distillation. The total content of metallic impurities (mainly Cu, Al, Fe and Gd) in distilled yttrium was less than 0.037 at%, the total content of nonmetallic impurities (mainly O,N and C) was less than 0.012 wt% in distilled and less than 0.008 wt% in double distilled yttrium. The samples for measurements were prepared by an electrospark method. After being cut, they were etched in a solution of nitrogen acid in dewatered ethyl alcohol in order to remove any deformed external layer.

An equipment used in our work made measurements of Young's modulus $E$ and internal friction $Q^{-1}$ possible at frequencies $10^2 - 10^4$ Hz, in the temperature region 4.2 - 400 K. The technique of experiment has been described earlier [21]. The yttrium samples for our investigations were thin bars 8.0 mm long and 0.1 - 0.2 mm thick, similar for all the specimens. The long axes of three samples were parallel to the c-axis (sample C) and laying in the basal plane (sample B) for the single crystal and coincided with the main texture direction (a-axis) for purified polycrystalline yttrium (sample T). Auto-vibrations of the samples were excited by an electrostatic method. The modulus $E$ was determined by the frequency of vibrations and dimensions of samples. The value of $Q^{-1}$ was determined by a number of damping oscillations between two certain levels of amplitudes after breaking off feed-back circuit. The absolute error in Young's modulus was ±6% and relative (from point to point) ±0.03%. Internal friction was defined with an accuracy of ±3%. The temperature was measured by a conventional copper-constantan thermocouple with a precision of ±0.5 K.

3. Results and Discussion

Figures 1 and 2 show the temperature dependence of Young's modulus and internal friction for Y single crystals in the basal plane and along the unique axis, respectively. Internal friction is fairly small at low temperatures, and generally increases with temperature. The increase becomes dramatic above 320 K. The $Q^{-1}(T)$ curve passes through a sharp maximum near 320 K for the sample in the basal plane. As for the sample along the c-axis, internal friction at high temperatures was so large that its correct measurements were not possible with our equipment. Weakly pronounced maxima of internal friction have also taken place at about 120 K for both samples. $E(T)$ curves tend to zero with zero slope in agreement with the Debye model and monotonically decrease with temperature. An extrapolation of the $E(T)$ curves to zero temperature gives $E_{0\text{bp}} = 134.0$ GPa for the basal plane and $E_{0c} = 51.1$ GPa for c-axis. Such a great difference in values of the modulus in various crystallographic directions points out a large anisotropy of the physical properties of yttrium. The smooth behavior of Young's moduli is disturbed at about 320 K simultaneously with a sharp increase of internal friction. At this temperature the $E(T)$ curves abruptly drop from near linear dependence, but the curves tend to come back to the same former temperature derivative also above 400 K. The temperature dependence of Young's moduli also demonstrates a weak but clear change of slope in the curves in the region 120 - 150 K (see, for example, inset in Fig. 2). The curves $E_b(T)$ and $E_c(T)$ have very small temperature hysteresis in the whole temperature region covered whereas the dependence $Q^{-1}(T)$ is accompanied by considerable thermal hysteresis above 320 K. The described behavior of Young's moduli and internal friction at high temperatures is characteristic for processes of relaxation of defects and dislocations of a crystalline structure. Thermal hysteresis in $Q^{-1}(T)$ curves indicates that the processes mentioned are metastable.

Figure 3 displays the temperature dependence of Young's modulus and internal friction for purified textured yttrium. The modulus monotonically decreases with temperature from
Fig. 1. — Temperature dependence of Young’s modulus and internal friction for single crystal yttrium in the basal plane.

Fig. 2. — Temperature dependence of Young’s modulus and internal friction for single crystal yttrium along the c-axis. Inset. Temperature dependence of Young’s modulus in the region 100-200 K.

\( E = 165 \) GPa at \( T = 4.2 \) K to \( E = 150 \) GPa at room temperature \( T = 293 \) K. A somewhat thermal hysteresis takes place above 170 K in Young’s modulus and above 200 K in internal friction. The abrupt increase of internal friction above 270 K is accompanied by a change of slope of the \( E(T) \) curve and is connected, as for the single crystal, with the relaxation of defects and dislocations in the material. Internal friction also demonstrates an anomalous behavior in the area 30-50 K (inset in Fig. 3). Such a behavior has no reasonable interpretation yet.
A careful study of Young’s modulus and internal friction of polycrystalline yttrium of technical purity gave a similar shape of the $E(T)$ curve to that for high pure textured yttrium. However, the absolute value of Young’s modulus for polycrystalline material is sometimes less and deceases from $E = 60.9$ GPa at 4.2 K to $E = 56.5$ GPa at 293 K. Such a dramatic difference in the moduli for single crystals, textured sample and polycrystalline sample of yttrium is connected with the large crystallographic anisotropy of elastic properties of the metal. Internal friction for polycrystalline sample of technical purity Y is also shown in Figure 3 for comparison.

It was interesting to analyze the elastic moduli data obtained in boundaries of the Debye model. The phenomenological model [23], considering the crystalline lattice of solid body as a statistical quantum ensemble of unharmonic oscillators, gives an expression for the temperature dependence of the lattice part of Young’s modulus:

$$E(T) = E_0(1 - KF(T/\Theta_D)),$$

(1)
where

\[ F(T/\Theta_D) = 3 (T/\Theta_D)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{\exp(x) - 1}, \]

and

\[ K = 9\alpha_\infty \Theta_D (Lc_1/c). \]

Here \( E_0 \) is Young's modulus at \( T = 0 \), \( \Theta_D \) is the Debye temperature, \( \alpha_\infty \) is the coefficient of heat expansion at \( T \to \infty \), \( c \) and \( c_1 \) are constants, describing respectively harmonic and unharmonic parts of the Hamiltonian of an oscillator, and \( L \) is a suitable dimensional parameter. As will be seen below, equation (1) describes well the experimental dependence \( E(T) \) in a wide region of temperatures.

At low temperatures \( (T \ll \Theta_D) \) the relative decrease of Young's modulus \( \Delta E \) is described by the following expression:

\[ \Delta E = (E - E_0)/E_0 = -KF(T/\Theta_D) \approx -\frac{\pi^4}{5}K(T/\Theta_D)^4. \]

At high temperatures \( (T \gg \Theta_D) \)

\[ \Delta E \approx -KT/\Theta_D. \]

Indeed, experiments show an approximately linear dependence of Young’s modulus on the temperature at relatively high temperatures \( (T \geq \Theta_D) \) in accordance with equation (5). As to the proportionality \( \Delta E \sim T^4 \) predicted by equation (4) at low temperatures, its verification requires highly accurate experiments and is difficult.

Because \( \Delta E \) is linearly proportional to the function \( F(T/\Theta_D) \) (see Eq. (1)), the experimental quantities \( \Delta E \) can be used for the computation of \( K \) and \( \Theta_D \). Our calculations were made in this way. First, the values \( F(T/\Theta_D) \) were computed for measured temperature points at a certain initial Debye temperature \( \Theta_D \).

Then the dependence of \( \Delta E(T) \) on \( F(T/\Theta_D) \) was fitted by a straight line with the least-squares method. The resulting values \( K \) and \( \Theta_D \) were determined by changing the Debye temperature as variable parameter by least mean square error of successive linear regressions. The results of computer calculations are presented in Table II.

**Table II. — Values of Young's modulus \( E_0 \) and \( E_{300} \) at \( T = 0 \) and \( T = 300 \) K, respectively, the constant \( K \) and the Debye temperature \( \Theta_D \) for single crystals along the c-axis (sample C) and in the basal plane (sample B), purified textured-with main direction of texture along the a-axis (sample T)—and technically pure polycrystalline (sample P) samples of yttrium. All data were averaged at decrease and increase of temperature.**

<table>
<thead>
<tr>
<th>The sample of Yttrium</th>
<th>( E_0 ) (GPa)</th>
<th>( E_{300} ) (GPa)</th>
<th>( K ) (abs.units)</th>
<th>( \Theta_D ) (K)</th>
<th>( Q^{-1} ) exp</th>
<th>( 10^{-4} ) calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>51.1</td>
<td>45.4</td>
<td>0.042</td>
<td>98</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>133.8</td>
<td>120.9</td>
<td>0.052</td>
<td>133</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>T</td>
<td>165.0</td>
<td>149.2</td>
<td>0.144</td>
<td>200</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>P</td>
<td>60.9</td>
<td>56.3</td>
<td>0.080</td>
<td>235</td>
<td>10</td>
<td>14</td>
</tr>
</tbody>
</table>
As was pointed out above, there is an anomalous behavior of Young’s modulus and of internal friction in the temperature regions approximately 120 – 150 K and above 320 K for the single crystals and above 270 K for purified and for technical purity yttrium (Figs. 1-3). Features of some physical properties of yttrium at the temperature regions mentioned were reported previously. Thus, anomalies were observed in the lower temperature region in references [7, 14] where the Hall effect and elastic constants were studied, respectively. In this temperature interval, the temperature derivative of the Seebeck coefficient changes its sign too [9]; this is an evidence for a change of the electronic structure of the metal at these temperatures. Studies of internal friction and shear modulus $G$ at frequencies ~ 1 Hz reported in references [15, 16] show their anomalous behavior in the higher temperature interval. These anomalies were connected with Zener’s processes [24] of relaxation of defects of crystalline structure due to interstitial gaseous impurities. Similar relaxation processes were observed earlier in dysprosium [22, 25].

The results of estimations of limiting values of internal friction due to thermoelastic mechanism [24] at 300 K are presented in Table II too, in comparison with experimental values of $Q^{-1}$. One can see that this mechanism can be essential far from maxima of internal friction determined by other reasons and should be taken into account when analysing $Q^{-1}$ data.

In conclusion, Young’s modulus and internal friction have been studied in detail in a wide temperature range for both single crystals and polycrystalline samples of yttrium of various purity degrees. The temperature dependence of Young’s modulus was found to be in general agreement with theoretical predictions for all samples. A strong anisotropy of the elastic and inelastic properties of yttrium has been observed. A number of additional anomalies have been found in the $E(T)$ and $Q^{-1}(T)$ curves in the temperature ranges of 30 – 50 K, 120 – 150 K and above 270 – 320 K. As high temperature features can be obviously connected with relaxation processes of defects and dislocations of crystalline lattice, anomalies at lower temperatures have no reliable interpretation yet and understanding of their nature needs a further careful study of the electronic and crystalline properties of yttrium.

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