Temperature Dependence of the Orthorhombic Asymmetry of Gallium Metal

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Precision strain-gauge measurements of the basal-plane lattice asymmetry \((a-b)/(a+b)/2\) in gallium metal have been made in the temperature range \(190 \text{ K} < T < 300 \text{ K}\). When analyzed in conjunction with previously published data these results indicate that the asymmetry is positive from the melting point, \(T_M \approx 303 \text{ K}\), down to at least 2 K. The asymmetry reaches a limiting value of \(5750 \times 10^{-6}\) at low temperatures and is decreasing rapidly toward zero near \(T_u\). The extrapolated ‘tetragonality’ temperature is \(T^* \approx 354 \text{ K}\).

Introduction

From its melting point at \(T_M \approx 303 \text{ K}\) down to at least 2 K gallium metal exists in a stable, face-centered orthorhombic crystal structure. In the most widely used naming convention for the crystal axes the lattice parameters at room temperature satisfy the inequality

\[ c > a > b. \]  

(1)

The atomic positions in the unit cell are given by the standard positions of \(D_2^{18}\) if these parameters are reassigned as \([z, x, y]\) in the usual notation (International Tables for X-ray Crystallography, 1952).

At room temperature the lattice parameters \(a\) and \(b\) are nearly identical,

\[ (a-b) \approx \frac{1}{1000} \left( \frac{a+b}{2} \right), \]

a fact which has led to periods of confusion in the literature regarding the relative size of \(a\) and \(b\) as a function of temperature (Barrett, 1962; Pearson, 1967; Barrett & Spooner, 1965). In this paper we report precision measurements of the quantity

\[ \varepsilon_{ab}(T) = \frac{a(T)-b(T)}{(a+b)/2} \]  

(2)

over the temperature range \(190 \text{ K} \leq T \leq 300 \text{ K}\). These data were obtained by a direct differential strain-gauge technique having a resolution of \(\delta \varepsilon_{\text{RES}} \approx 10^{-7}\) and reproducibility \(\delta \varepsilon < 10^{-6}\).

Sample preparation

The gallium samples used for the present measurements were obtained from large, cylindrical, single crystal boules grown by a seeded Bridgman method from 99.999% starting material. The boules were 19 mm in diameter and between 30 and 50 mm in length with the melt being seeded such that the cylinder axis lay within a few degrees of the crystalline \(c\) direction.

The strain-gauge samples, in the form of cubes approximately 1 cm on a side, were sectioned from the main boule with a diamond-wire saw and abrasive slurry. The cube faces were aligned to the crystal axis to better than 1° by Laue back-reflection, and the surfaces lapped on 600 grit aluminum oxide abrasive paper with ice water as a coolant and lubricant.

Following the lapping operation, the crystals were examined for surface cold-working on an X-ray crystal orien ter. Illuminating a small area (\(\approx 1 \text{ mm square}\)) of the face in question made it possible to survey the surface for misoriented material. A characteristic reflection of the axis being surveyed was maximized, the crystal was then translated and a new section of the crystal face was examined. The reflection was again maximized by reorienting the crystal. In this way a table of angular deviations versus X-ray beam position could be made. Typical deviations for the as-lapped face were of the order of \(\pm 15\) minutes of arc. The sample was then given a light room-temperature etch after which there was no measurable surface imperfection. Crystals prepared in the same manner and examined on a high-resolution X-ray diffractometer showed no significant diffraction-spot broadening beyond the instrument’s 100 arc second resolution.

Experimental method

Because of the near equality between \(a\) and \(b\) it is extremely difficult to determine the asymmetry \(\varepsilon_{ab}(T)\) with good precision from individual lattice-parameter measurements. The most reliable information to date has been the single-crystal thermal-expansion data reported by Powell (1951).

In the present case, the differential thermal expansion between the \(a\) and \(b\) axes was obtained directly by monitoring the differential change in resistance of two strain-gauge elements.

The strain gauge employed for the \(\varepsilon_{ab}(T)\) measurements is a Micro-Measurements\(^\dagger\) model WK-00-062TT-350, a dual-element foil-type gauge laminated onto an epoxy-fiberglass backing. The two elements are oriented with their strain-sensitive directions at right angles with each foil pattern occupying an area of \(1.6 \times 1.9 \text{ mm}\). The gauge is cemented to the sample

\[ \dagger \text{Micro-Measurements Co., Romulus, Michigan 48174.} \]
with Eastman* 910 FS fast-setting cyanoacrylate adhesive and Eastman 910 Surface Activator. The gauge and exposed glue line are then coated with polyurethane varnish to protect the cured bond from deterioration. Eastman 910 proved to be the only adhesive that gave the necessary shear strength without requiring an elevated cure temperature; however, it also set the lowest temperature, \(-75^\circ\text{C}\), to which measurements could be made.

In the present case the gauge is mounted on a c-axis sample face and the two elements aligned with the a and b crystal axes. The two elements are connected as opposing arms of a stable DC-excited Wheatstone bridge such that the bridge unbalance is proportional to the difference of the strains applied to the two elements. A recorder plot of bridge unbalance versus temperature gives the raw relative strain data from which \(\varepsilon_{ab}\) is calculated. The details of this calculation are described in Appendix I.

**Results and discussion**

The raw experimental results, after the correction procedure given in Appendix I, are in the form of relative strain, \(E(T - T_{\text{REF}})\), where

\[
E(T - T_{\text{REF}}) = \varepsilon_{ab}(T) - \varepsilon_{ab}(T_{\text{REF}})
\]

and \(T_{\text{REF}}\) is an experimentally selected reference temperature. These relative strains were then placed on an absolute scale by normalizing to a precision X-ray diffractometer measurement of the lattice parameters which gave

\[
\begin{align*}
a(298.0 \text{ K}) &= 4.526935 \pm 0.000041 \text{ Å}, \\
b(298.0 \text{ K}) &= 4.521224 \pm 0.000034 \text{ Å}, \\
c(298.0 \text{ K}) &= 7.663113 \pm 0.000071 \text{ Å}.
\end{align*}
\]

In the analysis of the data the asymmetry at \(T = 298\) K was assigned the value

\[
\varepsilon_{ab}(298 \text{ K}) = 1262.4 \times 10^{-6}.
\]

The results of two independent sets of measurements with different samples and strain gauges are shown in Fig. 1, and, on an expanded temperature scale, in Fig. 2.

These figures also show all previously published data on \(\varepsilon_{ab}(T)\), including the data of Bradley (1935), Powell (1951), Barrett (1962), Barrett & Spooner (1965), and Swanson & Fuyat (1953), as well as a series of unpublished results derived from X-ray powder diffractometer data on the angular splitting of the 153 and 513 reflections (Storm, Haemmerle & Lastovka, 1971).

Over the range of temperatures covered by the strain-gauge data the \((a - b)\) splitting can be represented to within the experimental error by a three-term power series

\[
\varepsilon_{ab}(T) = A_0 + A_1(T - T_0) + A_2(T - T_0)^2
\]

where \(T_0\) was arbitrarily chosen to be the midpoint of the temperature span of the data. For the measurement runs Nos. 74 and 76 shown in Figs. 1 and 2 the best-fit values of the parameters are

**No. 74**

\[
\begin{align*}
T_0 &= 245.0 \text{ K}, \\
A_0 &= 2360.5 \pm 3.0 \mu\text{e}, \\
A_1 &= -20.167 \pm 0.074 \mu\text{e K}^{-1}, \\
A_2 &= -0.0162 \pm 0.0003 \mu\text{e K}^{-2}.
\end{align*}
\]

**No. 76**

\[
\begin{align*}
T_0 &= 245.0 \text{ K}, \\
A_0 &= 2360.5 \pm 3.0 \mu\text{e}, \\
A_1 &= -20.130 \pm 0.046 \mu\text{e K}^{-1}, \\
A_2 &= -0.0130 \pm 0.0018 \mu\text{e K}^{-2}.
\end{align*}
\]
where both the coefficients and $\varepsilon_{ab}$ have been expressed in units of microstrain; $1 \mu e = 10^{-6}$. The standard deviations between fitted and measured strain values were 2.3 and 1.5 $\mu e$ respectively.

As is evident from Fig. 1 the asymmetry $(a-b)$ is positive over the entire range of temperatures in which measurements have been made. The distortion $\varepsilon_{ab}$ reaches a limiting value $\varepsilon_{ab} \approx 5750 \mu e$ at low temperatures and is decreasing rapidly toward zero as one approaches the melting point, $T_m \approx 303$ K. If the power series of (6), (7) and (8) are extrapolated to higher temperatures the indicated 'tetragonality' point, $\varepsilon_{ab} = 0$, occurs at

$$T^* = 353.8 \pm 1.0 \text{ K} \quad (9)$$

or approximately 50 K above the melting point. If all measurements shown in Fig. 1 are included in a single power-series fit, the $(a-b)$ difference can be adequately represented over the temperature range $0 \leq T \leq 303$ K in the form

$$\varepsilon_{ab}(T) = B_1(T^* - T) + B_2(T^* - T)^2 + B_3(T^* - T)^3 \quad (10)$$

with

$$B_1 = 22.17 \mu e \text{ K}^{-1}$$
$$B_2 = -1.373 \times 10^{-3} \mu e \text{ K}^{-2}$$
$$B_3 = -4.285 \times 10^{-5} \mu e \text{ K}^{-3} \quad (11)$$

and an intercept temperature

$$T^* = 354.14 \text{ K}. \quad (12)$$

With respect to the extrapolated zero-asymmetry temperature, it is interesting to note that gallium metal has an abnormally low melting point relative to the value expected from the usual correlation formulas. For example, the Lindemann correlation between the Debye temperature and the melting temperature for the elemental metals (Zemansky, 1957) would suggest that gallium should melt at about 800 K. In this regard, one can speculate that an impending structural transition at $T = T^*$ results in the destabilization of the crystalline phase with the liquid state energetically favored over a high-temperature, possibly tetragonal, solid phase.

The authors would like to thank R. L. Barns for performing the precision lattice-parameter measurements quoted in equation (4).

APPENDIX

In order to derive precise strain or expansivity data from strain-gauge measurements one must account for certain non-ideal characteristics of these sensors. In the simplest approximation a foil-type gauge element exhibits a fractional resistance change with applied strain given by

$$\frac{\Delta R}{R_0} = F \varepsilon \quad (12)$$

where the gauge factor, $F$, has a typical value $F \approx 2$. A more rigorous result that is observed to fit the behavior of real foil elements quite precisely is

$$\frac{\Delta R}{R_0} = F_1 \varepsilon_1 + F_2 \varepsilon_2 + F_{app} \varepsilon_{app}(T) \quad (13)$$

where $\varepsilon_1$ and $\varepsilon_2$ are the strains applied parallel to and perpendicular to the principal axis of the element (Micro-Measurements Technical Note, undated). The term $\varepsilon_{app}(T)$, the 'apparent' strain, is used to characterize the resistance change with temperature that is observed when the gauge is mounted on a substrate having zero thermal expansivity. (13) is commonly written as

$$\frac{\Delta R}{R_0} = F[\varepsilon_1 + K \varepsilon_2] + F_{app} \varepsilon_{app}(T) \quad (14)$$

where $K$, the 'transverse sensitivity', is the ratio of transverse and longitudinal gauge factors. The quantity $K$ is typically small, $K \approx 0.01$, and can be of either sign.

If two elements, each described by (14), are connected as opposing arms in an equal-arm Wheatstone bridge, the observed unbalance voltage is

$$AV = \frac{V_b}{4} \left\{ F(2)[\varepsilon(2)+K(2)\varepsilon(2)] + F_{app}(2)\varepsilon_{app}(T; 2) - F(1)[\varepsilon(1)+K(1)\varepsilon(1)] - F_{app}(1)\varepsilon_{app}(T; 1) \right\} \quad (15)$$

where $V_b$ is the applied bridge voltage. For the gauge used in the present measurements the apparent strain terms cancel exactly; furthermore, since the two elements are oriented with their principal axes at right angles, we have $\varepsilon_1(1) = \varepsilon_2(2)$ and $\varepsilon_2(1) = \varepsilon_1(1)$.

For the $\varepsilon_{ab}(T)$ measurements the strain gauge was mounted such that the principal axes of elements (1) and (2) coincided with the crystalline $b$ and $a$ directions respectively. In this case, if the bridge is in balance at a particular temperature $T_0$, the unbalance voltage at temperature $T$ is given by

$$AV(T) = \frac{V_b}{4} \left(1.99\right) \left\{ [\varepsilon_{ab}(T) - \varepsilon_{ab}(T_0)] ight. \right.$$  
$$\left. - 0.00960\varepsilon_{b}(T; T_0) - 0.03060\varepsilon_{a}(T; T_0) \right\} \quad (16)$$

where we have inserted the numerical values of the sensitivity factors for our particular gauge. The various lattice 'strains' in (16) are

$$\varepsilon_{ab}(T) = \frac{(a(T) - b(T))}{(a + b)/2}$$
$$\varepsilon_{b}(T; T_0) = \frac{b(T) - b(T_0)}{b(T_0)}$$
$$\varepsilon_{a}(T; T_0) = \frac{a(T) - a(T_0)}{a(T_0)} \quad (17)$$

In order to extract the desired relative orthorhombic distortion $[\varepsilon_{ab}(T) - \varepsilon_{ab}(T_0)]$ from the measured un-
balance voltage we need to know the individual lattice expansions $\varepsilon_\alpha$ and $\varepsilon_\gamma$. In analyzing the present results these quantities were obtained from the expansivity data of Powell (1951). Although the latter are not high-precision data, the relevant correction terms in (16) in which they are used contribute less than 3% to the measured $\Delta V(T)$.

References
