Structure of Thallium and Gadolinium at Low Temperatures

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X-ray diffraction at temperatures from 300°K to 5°K has been employed to search for a low-temperature transformation in thallium that might account for the anomaly in the pressure coefficient of the superconducting transition temperature of this element. No evidence of instability of the normal close-packed hexagonal structure was obtained either after cooling or after cold work at various low temperatures. Similarly, the close-packed hexagonal structure of gadolinium was found to be stable to 5°K.

I. INTRODUCTION

AN interest in determining the structure of thallium at low temperatures stems from the divergent results obtained in different laboratories in the measurement of the change in the superconducting transition temperature with hydrostatic pressure.[1] With results from various laboratories differing both in magnitude and sign, yet with mild plastic deformation apparently making no change in the behavior of a sample,[1] the question of a possible phase change during some of the tests immediately arose. Recent measurements by Hatton[2] again suggest a possible phase change in that they show the novel feature of a change in sign of the pressure coefficient of the superconducting transition temperature near 1200 kg/cm^2.

On the other hand, no evidence of a transformation is seen in Swenson's[3] measurements of total hydrostatic compression under 10 000 atmospheres over the temperature range from 4.2 to 300°K, and of thermal expansion at 0 and 10 000 atmospheres pressure over the same temperature range.

It was felt desirable to look also for a transformation in gadolinium, since it was thought possible that the hexagonal close packing might be competitive with, say, cubic close packing in some temperature ranges, as it is in cold-worked lithium,[4] even though prior workers have reported only the hexagonal form.[5,6]

II. EXPERIMENT

Each sample investigated, which was in the form of a polycrystalline lump, was inserted in the specimen holder of the cryostat on a low-temperature x-ray spectrometer described elsewhere,[4] which recorded the diffraction pattern with filtered CuK_α radiation. Radiation shields at 5°K and 78°K, respectively, surrounded the specimen, and a stainless-steel rod with a chisel-shaped end could be brought into position to cold-work the specimen.

To increase the probability of obtaining a transformation, especially if it were of the usual type found at low temperatures, i.e., martensitic, the samples were annealed before cooling and were also cold-worked at various low temperatures.

A. Thallium

The thallium sample was obtained from the American Smelting and Refining Company and was accompanied by the following "typical analysis" in weight percent: Pb 8×10^{-3}; Cu 7×10^{-3}; Cd 4×10^{-3}; Fe 10^{-4}; Bi less than 10^{-4}. It was a portion of a piece studied by Swenson,[3] who found that the ratio of the resistivity of the piece at 300° to that at 4.2°K was 875. Specific tests were as follows, all conducted in a vacuum of 5×10^{-6} mm Hg or better.

Run No. 1: Cold-worked at 25°C and annealed at this temperature 3 days; x-rayed; cooled to 78°K and x-rayed; cooled to 5°K and x-rayed; cold-worked at room temperature and x-rayed.

Run No. 2: Annealed at 100°C for 15 min and x-rayed at room temperature; cooled to 78°K and x-rayed; cooled to 5°K and x-rayed; cold-worked at 5°K and x-rayed; warmed to 96°K and x-rayed; warmed to 120°K and x-rayed; warmed to 24°C and x-rayed; cold-worked at 24°C and x-rayed; annealed at 24°C for 4 days and x-rayed.

Run No. 3: Cold-worked at 24°C and x-rayed; annealed at room temperature 2 days and x-rayed; cooled to 78°K and x-rayed; cold worked at 78°K and x-rayed; cold-worked at 5°K and x-rayed; warmed to 24°C, annealed for 3 days and x-rayed.

Run No. 4: A sample was filed at room temperature and its diffraction pattern was recorded on a commercial spectrometer within the first few hours after filing and again after 40 hours at room temperature.

The diffraction patterns recorded by a Geiger counter and recorder during these runs were studied carefully for evidence of a transformation induced by cold work or by cooling. It was found that the close-packed hexagonal structure remained untransformed by these various low-temperature treatments.

On some runs with an annealed sample, a few extra reflections were recorded which were reduced or removed by cold work at any of the temperatures listed above and which were absent in the pattern of the filings. Various tests proved that these did not arise

[1] M. D. Fiske, Phys. Rev. **94**, 495 (1954).
[2] J. Hatton, Phys. Rev. **103**, 1167 (1956).
[3] C. A. Swenson (private communication).
[4] C. S. Barrett, Acta Cryst. **9**, 671 (1956).
[5] S. Sekito, Z. Krist. **74**, 189 (1930).
[6] H. Lipson and A. R. Stokes, Nature **148**, 437 (1941).

from a low-temperature phase of thallium, and therefore they do not influence the conclusions we have drawn regarding the low-temperature stability of thallium.

Lattice constants are listed below as determined by graphical plotting and extrapolation, using the Nelson-Riley function with successive approximations of the c/a value. All runs were made on the polycrystalline sample in the low-temperature equipment except the last one listed, which was made on a commercial unit (XRD-3) using filings and extending to $2\theta=163°$ instead of 108° as in the other records. The accuracy of the individual values was limited by the inaccessibility of the high-angle peaks; it is estimated to be ± 0.03 to 0.05%. The figures are in angstroms, based on the CuK_α wavelength 1.54178 A.

Tl at 5°K after cold-work at 78° and 5°K:

$a=3.438$, $c=5.478$, $c/a=1.593$.

Tl at 78°K after cooling from anneal at 100°C:

$a=3.437$, $c=5.478$, $c/a=1.594$.

Tl at 80°K after cold-work at 80°K:

$a=3.437$, $c=5.478$, $c/a=1.594$.

Tl at 96°K after cold-work at 5°K:

$a=3.439$, $c=5.481$, $c/a=1.594$.

Tl at 23°C after cold-work at 23°C:

$a=3.455$, $c=5.519$, $c/a=1.597$.

Tl filings at 28°C:

$a=3.456$, $c=5.525$, $c/a=1.598$.

For comparison we note that Lipson and Stokes[6] obtained $a=3.4496\pm0.0002$, $c=5.5137\pm0.0004$ A, $c/a=1.5984\pm0.0001$ at 18°C.

B. Gadolinium

A sample of gadolinium of 99.6% purity was used in polycrystalline form. The chief impurities were Mo, Fe, Sm, O_2, N_2, Eu, and Ta; there were also traces of F, Mn, B, Si, Pb, and Mg.

The sample was forged to appropriate shape at room temperature, annealed 15 minutes at 800°C and etched. X-ray diffraction patterns were run after cooling to liquid nitrogen temperature, then at 5°K after cold-working the sample at this temperature, and after a second cold-working at this temperature.

Nine diffraction peaks were obtained; all of the peaks at each temperature could be accounted for as due to the normal close-packed hexagonal structure[7]; they were the 002, 101, 102, 110, 103, 112, 004, 105, and 302. The intensity of the peaks indicated that the cold-work had produced some degree of preferred orientation, with the basal plane tending to be parallel to the specimen surface. Since high-angle reflections were not obtained, a precision value for the lattice constants could not be computed, but no important deviation from prior values[7] was evident.

III. CONCLUSIONS

Although thallium has an anomaly in the pressure coefficient of the superconducting transition temperature at pressures near 1200 kg/cm², no evidence of instability of the hexagonal close-packed phase at zero pressure was disclosed in these diffraction patterns made after cooling to temperatures in the liquid nitrogen and liquid helium range, or after cold-working at these temperatures. Gadolinium also retained its hexagonal structure in similar experiments. It is therefore concluded that the hexagonal structure of these elements is stable down to 0°K, and that any anomalies observed cannot be ascribed to transformations of a sort to be detected by the usual diffraction methods.

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[7] Banister, Legvold, and Spedding, Phys. Rev. 94, 1140 (1954).