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Thermal Expansion of Bismuth Single Crystals Near the Melting Point

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Single crystals of Bi *highly purified* by repeated crystallizations show no decline in the coefficient of thermal expansion as the melting point is approached. It is shown that the presence of impurities (Pb, Ag, Cd, Sn) in very small amounts does cause the coefficient to decline and attain negative values in a range of 10° or 20°C below the melting point. On the basis of these observations the discrepancy between previous results by Roberts, and Ho and Goetz concerning the integral (macroscopic) thermal dilatation, and Goetz and Hergenrother, and Jay concerning the lattice expansion of Bi crystals is discussed.

Introduction

One of the major problems of the solid state is the phenomenon of melting. The characteristics of this phenomenon for a crystalline material have not been satisfactorily included in the theories of the crystalline state. It is expected that some information concerning the process of melting could be obtained by studying the physical properties of materials at temperatures near their melting points.

In this investigation the thermal expansion of bismuth single crystals was measured. Bismuth was chosen since earlier work indicated some anomalies in the thermal expansion near the melting point. Roberts[1] and Ho[2] found the thermal expansion macroscopically to decrease in a range of 10° to 30°C below the melting point. Roberts suggested that impurities may be important in causing the lowering of the expansion coefficient but did not state that impurities were known to be present in his crystals.

Determination by Goetz and Hergenrother[3] of the lattice spacing by refraction of x-rays indicated no decrease in the coefficient of thermal expansion as the melting point was approached. However, later measurements by Jay[4] on the crystal lattice spacing differed from those of Goetz and Hergenrother in that no divergence between the macroscopic and the lattice expansion coefficient was found and in that indications of a very rapid decline of the lattice expansion coefficient normal to the principal axis above 250°C were obtained. The powder method was used by Jay. The samples tested were filings from a metal rod which by analysis was given Bi, 99.995 percent; Ag, 0.004 percent; other elements, minute trace. From his measurements Jay concluded that there was no difference between the integral (macroscopic) expansion of a crystal obtained with a dilatometer and that indicated by the change of the atomic spacing within the crystal lattice as measured by x-ray diffraction for the range between room temperature and melting point.

Production of Crystals

The crystals used in this investigation were grown in the apparatus described by Hasler.[5] A vacuum pump was added to the apparatus and the crystals grown in high vacuum. They were at all times protected from mercury vapor by a liquid air trap.

The bulk bismuth used was purchased as commercially pure stock. To obtain very pure materials this was placed in a graphite mold ($1.2\times1.0\times25$ cm) and recrystallized five times. The total time for each crystallization of the rod about 20 cm long was 7 to 18 hours. After each crystallization pieces 2 to 4 cm long were broken off each end of the bar and the remaining material used for the next crystallization. This work and that of Hasler[6] supports the original findings of L. Schubnikof[7] that a large part of the impurities is driven along the molten metal ahead of the region of crystallization and finally deposited near the end of the crystal. After the

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* On leave from the University of Minnesota.

[1] J. K. Roberts, Proc. Roy. Soc. **A106**, 385 (1924).

[2] See A. Goetz and R. C. Hergenrother, Phys. Rev. **40**, 643 (1932); A. Goetz and T. L. Ho, Phys. Rev. **43**, 213 (1933); F. Blank, Phys. Zeits. **34**, 353 (1933).

[3] A. Goetz and R. C. Hergenrother, Phys. Rev. **40**, 643 (1932).

[4] A. H. Jay, Proc. Roy. Soc. **A143**, 465 (1934).

[5] M. F. Hasler, Rev. Sci. Inst. **4**, 656 (1933).

[6] Thesis, *The Thermo-electric Analysis of Micro-alloyed Single Crystals of Bismuth*, Cal. Inst. Tech. (1933).

[7] L. Schubnikof and H. T. de Haas, Comm. Univ. of Leyden No. 207c, page 26 (1930).

fifth recrystallization the material was cast in graphite molds (approximately 3×3×150 mm) in a vacuum induction furnace. These polycrystalline casts we shall call Bia. The pieces broken from the larger rod after each recrystallization were also cast in small bars in the induction furnace. This material we shall designate as Bib. The polycrystalline casts were seeded to obtain various orientations of single crystals. They were grown in the apparatus[5] mentioned above and in some cases were recrystallized three or four times to obtain further purification. Specimens 2 cm long were cut from various parts of the final single crystal rods 10 to 24 cm long and used in the dilatometer.

The Expansion Apparatus

The dilatometer is described in detail in a current issue of the *Review of Scientific Instruments*.[8] Its essential parts were an optical lever and a Moll thermorelay to detect the deflections of the light beam. The temperature was measured by means of a platinum resistance thermometer. Recording galvanometers were used so that a length-temperature curve was traced on 5″×7″ photographic paper. Some of the curves are reproduced in Fig. 1. The difference between this method and that which uses an ordinary dilatometer lies in the possibility of recording the thermal dilatation of a specimen over temperature intervals of only a few degrees with a considerable accuracy in spite of the large sensitivity.

Discussion of Results

The results indicate rather definitely that for pure bismuth crystals there is no decline in the coefficient of expansion up to within three degrees of the melting point. At 268.0 to 268.5° the gravitational load transgresses the elasticity limit of the crystals. This is indicated by the plastic deformation of the lower part of the crystal although occasionally intermediate regions showed this deformation

Typical temperature-length curves are shown in Fig. 1. Curve *A* is the record of a specimen cut from a crystal grown from Bia. The crystal was seeded so that the trigonal axis was perpendicular to the axis of the crystal (P_1 orientation). Except for a small decline in the last degree before collapse there is no change in the coefficient as the crystal is heated above 250°C. Curve *B* is the record of a section cut from the end of a crystal grown from Bib. It had the same orientation as the first crystal. The trace departs from a straight line at 263°C and the coefficient of expansion declines rapidly thereafter.

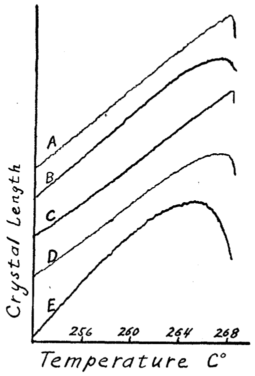

FIG. 1. Curves *A* and *C*; thermal expansion of crystals of pure bismuth. Curves *B*, *D* and *E*; thermal expansion of crystals containing impurities. Curves are displaced and various ordinate scales are used.

The crystal used to obtain curve *C* was a cast of Bia which was then recrystallized three times. The end of the material was discarded after the second crystallization and a middle section of the final crystal was used. The trigonal axis was parallel to the crystal length (P_3 orientation). There is no indication of decline of the slope of the line up to the point where the crystal collapsed.

During the course of the work crystals of various orientations were used and similar results obtained. The coefficient, of course, has different numerical values for the various orientations. No attempt was made to obtain precise absolute values of the coefficients. The measurements made agreed with the accepted values of the coefficients for the various orientations. The different slopes of the straight portions of the curves of Fig. 1 are not significant as the dilatometer was set for different sensitivities.

Curve *D* is the record of a section near the end (part of crystal last to solidify) of a very long (24 cm) crystal grown slowly (10 hrs.) from Bib. A middle section of this crystal gave a sharp break such as that in curve *C*.

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[8] A. Goetz, J. W. Buchta and T. L. Ho, Rev. Sci. Inst. **5**, 428 (1934).

The results on a score of crystals are all consistent with the assumptions that a small amount of impurity causes the decline of the coefficient near the melting point and that impurities in the molten metal are driven along ahead of the region of crystallization in the process of growing the crystals. In very pure Bi no indication of the approach to the melting point is given by the thermal expansion.

The expansion is evidently affected by *very small* amounts of impurities and their determination proved to be rather elusive. However, it was shown that small amounts of Pb, Ag, Sn and Cd were important. The results of a rough spectroscopic analysis of the specimen used for curves *A*, *B*, *C* and *E* are given in Table I.

TABLE I.

Crystal curve	Percent of impurities Pb	Cu	Ag	Cd	Ca	Al	Mg	Ti
A	0	0.001	0	—	0.1	—	—	—
B	0.05	0.01	0.05	—	0.1	0.001	0.001	0.001
C	0	0.001	0	—	0.1	0.001	0.01	0.01
E	0.001	0.1	0.01	1.0	0.1	—	—	—

Polarograph tests checked the values of the lead content. The traces of Ca, Al, Mg and Ti are probably mechanically included. The samples were tested after they had been melted in the dilatometer.

The decline of the curves for crystals containing impurities is partially but not entirely caused by plastic deformation. If the contraction near the melting point was not carried too far the crystal could be tested again. Curve *E*, Fig. 1, is a second record of a crystal containing some Cd that had been previously heated. Curve *F*, Fig. 2, is the trace obtained at the first heating. The curve departed from a straight line at a lower temperature in the first run than in the second. Some permanent deformation occurred and on cooling the curve was not retraced.

The specimens used for curves *G* and *H*, Fig. 2, have several percent of tin. Curve *G* was obtained on heating and curve *H* on cooling. The phenomenon in the temperature range indicated is at least partially reversible.

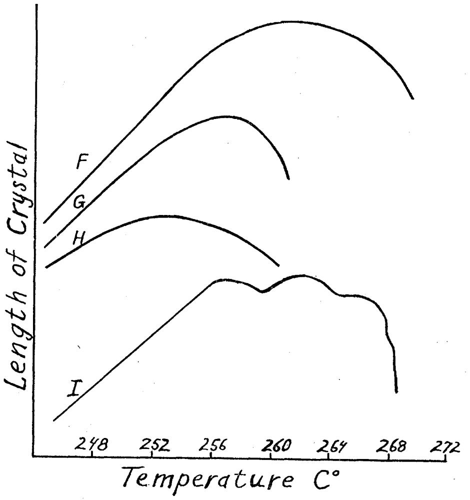

FIG. 2. Curve *F*; thermal expansion of a bismuth crystal containing Cd. Curves *G* and *H*; thermal expansion of a bismuth crystal containing Sn. *G*, heating; *H*, cooling. Curve *I*; thermal expansion of a bismuth crystal containing Ag.

It is believed that the present work explains some of the discrepancies of previous experiments, though perhaps not all. There exists evidently a process within the crystal which causes a decline of the expansion coefficient which is partially, at least, of reversible nature as soon as traces of impurities are present. This decline cannot be traced in the lattice expansion, at least the indications of such an effect found by Jay[4] could not be reproduced by recent tests more accurate than the original measurements by Goetz and Hergenrother.[3] Furthermore, the Bi used by Jay[4] was of an exceptionally high degree of purity (0.004 percent Ag), a concentration for which we should not expect a decline. In order to be certain about this and to decide whether or not the decline of the expansion coefficient characterizes only soluble (or partially soluble) admixtures (Pb and Cd being partially soluble in Bi) and not foreign atoms unable to interpenetrate the crystal lattice (e.g., Ag) a record of a specimen containing not more than 0.5 percent (atomic) Ag was made (curve I, Fig. 2). The Ag was added to Bi which had been purified so that it gave a sharp break in the curve at 268°C. The mixture was then recrystallized once and a center section of the crystal tested. The general characteristics of the curve—a contraction followed by an expansion—could be repeated on the same specimen by carefully heating and cooling it in the region above 256°C. The phenomenon seems to be in suggestive analogy to that described for the Bi-Pb crystals[9] in the region of the eutectic melting point since the corresponding point for the Bi-Ag system lies at 260°C. Since changes of this type apparently do not affect the regions of the lattice capable of diffraction, they should not be reflected in x-ray measurements.

Our observations establish thus a support for the hypothesis of "decrystallization" by Goetz and Hergenrother[2] which attributes any deviation of the macroscopic qualities from the crystal lattice as seen by x-rays to disturbances caused by foreign atoms even if they are soluble. The mentioned hypothesis suggests, however, a divergence of the two expansions (i.e., a decline of the macroscopic dilatation) even for ideally pure material. The present results do not disprove this possibility since the region of such a decline may be restricted to the very close neighborhood of the melting point which is inaccessible due to plastic deformation of the specimen in the gravitational field.

The authors are indebted to Dr. M. F. Hasler for the spectroscopic and polarographic analyses and to him and Mr. R. C. Kendall for aid in growing the crystals and valuable discussions during the course of the work.

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[9] A. Goetz, J. W. Buchta and T. L. Ho, Phys. Rev. **46**, 538 (1934).

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The Magnetostriction of Pure and Alloyed Bi Single Crystals*

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The existence of a magnetostrictive effect (Joule effect) in nonferromagnetic substances, first demonstrated by Kapitza for large transient fields, is here shown for steady fields of moderate (20 to 25 kg) values. Pure (99.97 percent) Bi single crystals and crystals with dissolved foreign atoms are used. A recording dilatometer permitted measurements of a change in length of 2.5×10^{-7} cm. The sum of errors amounted to approximately 10 percent. The modulus of magnetostriction (m) is defined by $\Delta l/l=\frac{1}{2}mH^2$. For pure Bi crystals $m=+5.7\times10^{-16}$ (elongation) parallel to trigonal axis and $m=-7.0\times10^{-16}$ (contraction) normal to trigonal axis. Bi crystals with Pb, Sn and Te in concentration within the solubility range were studied. Sn and Pb (electropositive) first cause the contraction normal to the trigonal axis to diminish and finally with increasing concentrations, cause an elongation, Sn being four times as effective as Pb. Parallel to the axis small concentrations of Sn decrease the elongation, larger concentrations increase the elongation. The effect of Pb in this direction is small. Te (electronegative) produced a much larger specific effect but no change in sign. The effect was of the same order of magnitude for the two principal crystal orientations. The data are discussed with special reference to the influence of foreign atoms on the magnetic susceptibility, studied previously by Goetz and Focke. It was found that the change of the stress coefficient of the susceptibility with the concentration of foreign atoms *normal* to the principal axis is inversely proportional to the concentration and furthermore: the variation of the stress coefficient with the concentration is nearly equal to the variation of the susceptibility at higher concentrations, in other words the stress coefficient of the susceptibility is proportional to the susceptibility itself. It is furthermore concluded that the results presented justify the previous assumption of the existence of two types of insertion of foreign atoms in the crystal lattice, i.e., selective adsorption for small concentrations and volume absorption for larger concentrations.

I. INTRODUCTION

THE search for magnetostrictive effects in non-ferromagnetic materials was begun soon after the discovery by Joule in 1847 of the effect in ferromagnetic materials. Aubel[1] in his review quotes a number of attempts[2–6] to detect the phenomenon. All gave negative results as did more recent work of Hobbie,[7] Schulze[8] and Bryan and Heaps.[9] Kapitza[10, 11] was the first

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[*] Partly contained in: A. Wolf, Thesis, Cal. Inst. of Tech. 1933; A. Wolf and A. Goetz, Phys. Rev. **43**, 213 (1933).

[1] Aubel, Phys. Rev. **16**, 60 (1903).

[2] S. Bidwell, Phil. Trans. **179**, 205 (1888).

[3] Grimaldi, J. de physique **8**, 552 (1889).

[4] Aubel, J. de physique **1**, 422 (1892).

[5] Knott, Nature **61** (1899).

[6] A. P. Wills, Phys. Rev. **15**, 1 (1902).

[7] J. R. Hobbie, Phys. Rev. **19**, 456 (1922).

[8] A. Schulze, Zeits. f. Physik **50**, 448 (1928).

[9] A. B. Bryan and C. W. Heaps, Phys. Rev. **37**, 466 (1931).

[10] P. Kapitza, Nature **124**, 53 (1929).

[11] P. Kapitza, Proc. Roy. Soc. **A135**, 537 (1932).