Preparation of essentially pure CrOOH was achieved in several of the experiments reported, for example 25, 26 and 28. The thermal analysis curve (Fig. 1c) is for material of almost theoretical composition. The average density of CrOOH as determined by the displacement method using a 1-cc. pycnometer on samples containing 61.0–61.2% Cr was 4.12 g./cc.

Discussion

X-Ray data for CrOOH indicate that it is not isomorphous with any of the isoformular aluminum, manganese or iron compounds. Iron and aluminum oxyhydroxides are isodimorphous, and groutite (α-MnOOH) also is isomorphous with diaspore and goethite[12] members of the alpha series. However, a second manganese oxyhydroxide, manganite, does not have the same unit cell as boehmite and lepidocrocite which are members of the gamma series[13]; also a third iron oxyhydroxide, β-FeOOH, has been reported.[14] A mineral having the composition CrOOH has been found[15] but from available data[16] it appears to give an X-ray diffraction pattern different from synthetic CrOOH. The arrangement of lines on the X-ray diffraction pattern of CrOOH is somewhat similar to the arrangement of lines in the patterns of lepidocrocite or boehmite, members of the γ-series. An elucidation of the structural relationships among these oxyhydroxides should prove to be a most interesting and important contribution to inorganic chemistry.

Although the data presented do not define stability relations in the system chromium(III) oxide–water, discussion of several experimental facts suggests probable relationships. CrOOH was formed in the hydrothermal bomb at temperatures below 419–424°, and is probably the stable phase below this temperature since it decomposed endothermically at 420–430° in the thermal analysis apparatus to give rhombohedral Cr_2O_3. The cubic oxide may perhaps be regarded as monotropic, as is the cubic gamma iron oxide, since differential thermal analysis curves of mixtures of CrOOH and cubic oxide did not show the second minimum which would be expected for a stable cubic oxide–rhombohedral Cr_2O_3 transition.

Phase relationships in which CrOOH is the stable phase below a transition temperature of 419–424°, rhombohedral Cr_2O_3 is stable above that temperature, and the cubic oxide is a metastable phase, are consistent with the data presented except for the serious difficulty that the rhombohedral oxide could not be converted to CrOOH.

ITHACA, NEW YORK RECEIVED DECEMBER 7, 1951

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[12] J. W. Gruner, *Am. Mineral.*, **32**, 654 (1947).

[13] M. J. Buerger, *Z. Krist.*, **95**, 163 (1936).

[14] H. B. Weiser and W. O. Milligan, THIS JOURNAL, **57**, 238 (1935).

[15] Abstract in *Am. Mineral*, **34**, 339 (1949).

[16] M. Fleisher and J. M. Axelrod, U. S. Geological Survey, private communication.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Diamagnetic Anisotropy of Natural and Synthetic Rubbers[1]

BY ELIZABETH WEIR TOOR[2] AND P. W. SELWOOD[3]

The change in anisotropy with elongation has been found for natural rubber and for several synthetic rubbers. Unsaturated rubbers have a large principal susceptibility perpendicular to the direction of stretching, because of the presence of olefinic double bonds. The differences between natural rubber and polybutadiene are attributed to the presence of unsaturated side-groups caused by 1,2-addition in polybutadiene. It is probable that the magnetic anisotropy of these rubbers depends not upon the actual degree of crystallinity of the rubbers, but upon the ability of the long-chain molecules to align themselves parallel to the direction of stretching. Therefore the changes in anisotropy with stretching will be large when there is no cross-linking, and small when cross-linking occurs to any large extent. Saturated rubbers have an anisotropy opposite in sign to that of unsaturated rubbers. This must be caused by the broadening of electronic orbits perpendicular to the direction of stretching. Apparently methyl side-groups cause such a broadening of electronic orbits in polyisobutylenes, an effect much greater than the similar effect in polyethylene.

Introduction

The magnetic anisotropy of rubbers has previously been studied by Mme. Cotton-Feytis.[4] She first observed that vulcanized commercial rubber showed some anisotropy and studied the effects of compression, stretching, and hot and cold working upon crude rubber. By Krishnan's oscillation method[5] she measured the anisotropy of stretched rubbers, using rubber bands stretched around a glass or plexiglas disc. The anisotropy was found to increase in the early stages of elongation, but at 400 to 500% elongation the anisotropy tended toward a limit, the curve of anisotropy as a function of tension having the same general shape as the curve showing variation in intensity of spots in the X-ray diffraction pattern of rubber with tension.[6]

In this work, the changes in diamagnetic anisotropy upon stretching have been measured for natural rubber and for several saturated and unsaturated synthetic rubbers in an attempt to relate the changes in anisotropy with stretching to the degree of orientation of the rubbers.

Experimental Part

Preparation of Samples.—The following rubber samples, and their descriptions, were supplied by the B. F. Goodrich Company, in the form of thin sheets approximately a millimeter thick, between two layers of cellophane. The samples were obtained through the courtesy of Dr. H. P. Brown.

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[1] This is the third paper from this Laboratory on the diamagnetic anisotropy of high polymers. The second, by Weir and Selwood, appeared in THIS JOURNAL, **73**, 3484 (1951).

[2] Award of the du Pont Company Postgraduate Fellowship in Chemistry is gratefully acknowledged.

[3] Inquiries concerning this paper should be addressed to P. W. Selwood.

[4] E. Cotton-Feytis, *Compt. rend.*, **214**, 485 (1942); **215**, 299 (1942).

[5] K. S. Krishnan, B. C. Guha and S. Banerjee, *Phil. Trans. Roy. Soc. (London)*, **A231** 235 (1933).

[6] S. D. Gehman, *Chem. Revs.*, **26**, 203 (1940).

Natural Rubber, No. 1 thin pale latex crepe, essentially a polyisoprene. Polybutadiene X-453, a 50% conversion polymer stabilized with phenyl β-naphthylamine, short-stopped with di-*t*-butylhydroquinone. Polybutadiene V, a 93% conversion polymer made at 50° and stabilized with 1.5% phenyl-β-naphthylamine, short-stopped with hydroquinone. Polybutadiene VI, a 73% conversion polymer made at 50° and stabilized with 1.5% phenyl-β-naphthylamine, short-stopped with hydroquinone. Butyl Rubber (GRI-50) a polyisobutylene containing about 2% of butadiene or isoprene. Vistanex, polyisobutylene of molecular weight about 100,000. Vistanex B-100, a polyisobutylene of molecular weight about 100,000. Vistanex B-120, a polyisobutylene of molecular weight about 120,000.

The rubbers were used as small rubber bands which could be fitted around a thin rectangular slab of an isotropic or nearly isotropic substance. This slab could then be attached to a suspension for the anisotropy measurement. By varying the size of these supporting slabs, the elongation of the rubber band could be changed. Polyethylene was chosen as the material for these cores, because it has a small anisotropy, is light, and because it is rigid enough that thin slabs will not buckle when holding a highly elongated rubber band. A series of small rectangular slabs of polyethylene were cut from a thin sheet of polyethylene supplied by B. F. Goodrich Company. The magnetic anisotropy of each slab was measured, and the dimensions of each were found with a micrometer caliper. Each slab was weighed also.

A small portion of each sheet of rubber was dissolved in benzene to make a cement for forming rubber bands. The rubber Polybutadiene V would not dissolve in benzene or other solvents and no rubber bands were made from this sheet.

A strip of rubber about one inch long and a half-inch wide was cut with scissors from the original sheet, avoiding any bubbles or other visible imperfections. The strip was laid upon a six-inch square glass plate and the cellophane layers on both sides were peeled off with an embroidery needle, care being taken not to stretch the rubber nor to mar the surface. By use of a sharp razor blade the strip was trimmed to the desired width, 3 to 5 mm. Then the smallest polyethylene core to be used was laid across the sample with the upper and lower ends protruding about 1 mm. over the side of the strip. The ends of the strip were trimmed with a razor until they just met about the polyethylene slab. The appropriate rubber solution was applied along the two edges to be joined. These edges were then brought together, and if necessary held together until they stuck. Then a thin coat of rubber solution was applied over the join, followed by one or two more coats at half-hour intervals. When the join had dried thoroughly, the band was removed from the polyethylene core with a small needle. One or two coats of rubber solution were then applied to the inner side of the join. When the rubber band had dried completely, it was ready for use, and it was assumed that on the polyethylene slab used in making the band, the rubber was unstretched.

Magnetic Anisotropy Measurements.—These were made by the Krishnan flip-angle method.[7] The equipment used and the application of the method to polymers have previously been described.[8] All magnetic measurements were made at room temperature.

The diamagnetic anisotropy of each rubber band was determined first on the polyethylene core used in making it, and then while stretched on successively larger cores. The size of the cores was limited by the necessity of having the sample hang freely in the glass tube protecting it. A number of the samples wore very thin or started to tear before the largest core was reached and the final measurements on each band were therefore less reliable than those made at lower elongations. It should be noted that the anisotropy measured was the difference between the susceptibility parallel to the direction of stretching and the susceptibility perpendicular to the direction of stretching of the rubber band.

Measurements were also made of the change in anisotropy with time, at one elongation, for natural rubber. The anisotropy was measured at one elongation after various time intervals, until the anisotropy reached a constant value. These measurements were then repeated at each of the higher elongations.

Results

In Table I are shown the magnetic anisotropy data for a typical sample of natural rubber.[9] The angle between the plane of the suspended sample and the direction of the field is given at each elongation. An angle of 0° indicates that the direction of stretching was parallel to the direction of the magnetic field when the sample was in its initial equilibrium position. The weight of the rubber band is also given.

TABLE I

MAGNETIC ANISOTROPY OF NATURAL RUBBER AT VARIOUS ELONGATIONS

Angle	Weight, mg.	ΔX/g. × 10^9 (observed)	ΔX/g. × 10^9 (corrected)	($\Delta X - \Delta X_i$)/g. × 10^9 (corrected)	Elongation, %
0°	15.00	59	97	0	0
0		88	139	43	20
0		109	155	58	57
0		142	186	89	96
0		193	247	151	151
0		268	417	320	259

The observed value of the anisotropy, ΔX per gram, is given at each elongation of the sample. The observed values were corrected for the anisotropy of the supporting polyethylene slabs, and for effects at the ends of the polyethylene slabs. These corrected values of the anisotropy per gram are given in the fourth column of the Table. The change in anisotropy at each elongation is listed as ($\Delta X - \Delta X_i$) per gram, where ΔX_i is the initial anisotropy of the unstretched sample. The per cent. elongation of the sample is given also, taking the elongation of the unstretched sample as 0%.

In Fig. 1 the change in anisotropy ($\Delta X - \Delta X_i$) per gram is plotted *versus* per cent. elongation for all samples of natural rubber and of butyl rubber. For each sample of each rubber the straight line of best fit was determined by the least squares method, and the intercepts and slopes found for all samples of each rubber were averaged to give a representative equation for each rubber. In Fig. 2 ($\Delta X - \Delta X_i$) per gram is plotted for each rubber using these averaged equations. Polyethylene, for which the change in anisotropy with elongation has previously been measured,[1] is included in this graph for comparison. In these graphs the curves for those rubbers which showed a larger susceptibility perpendicular to the direction of stretching have a positive slope, while the curves for the rubbers having a larger susceptibility parallel to the direction of stretching have a negative slope. The change of anisotropy with time was measured for two samples of natural rubber, and was found to be small.

A source of error was introduced into the measurements by uneven stretching of the rubber bands on the polyethylene cores, and by small rips in the samples, which occurred frequently at high elongations. Thus the actual elongation of a sample was not necessarily that which would be calculated

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(7) K. S. Krishnan and S. Banerjee, *Phil. Trans. Roy. Soc. (London)*, **A234**, 265 (1935).

(8) P. W. Selwood, J. A. Parodi and A. Pace, Jr., THIS JOURNAL, **72**, 1269 (1950).

(9) The complete results for all the rubbers measured are available in the Doctorate Thesis of E. W. Toor, Northwestern University Graduate School, 1951.

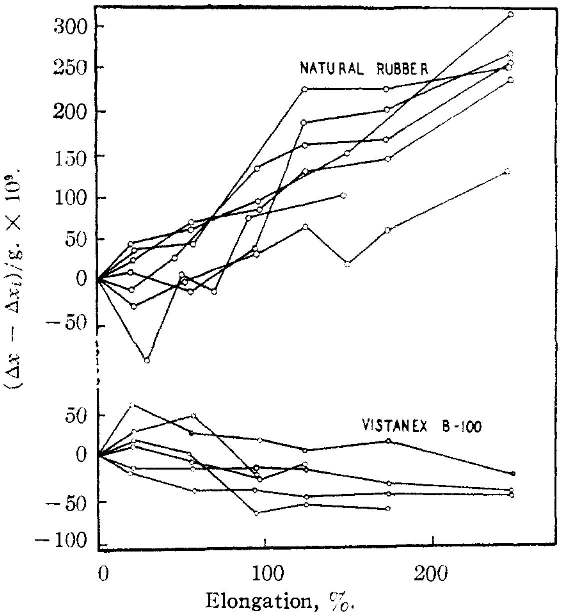

Fig. 1.—Corrected magnetic anisotropy of all samples of natural rubber and of Vistanex B-100 *vs.* % elongation, showing the variations in anisotropy from one sample to another of the same material.

from the size of the core used. The least squares method of finding the line of best fit adjusts only the anisotropy values, and not the elongations. However, the results obtained are an indication of the relative magnitudes of the anisotropy changes occurring with elongation for each of the rubbers.

Discussion of Results

The rubbers can be considered as uniaxial crystals, with the unique axis parallel to the direction of stretching. Bunn[10] reports that X-ray diffraction photographs of polyethylene indicate that the electron clouds of the $-CH_2$ groups are not spherical but are elongated in the plane of the carbon–hydrogen bonds, the plane normal to the chain axis. This distortion would lead to an increase in the mean square radii of the electronic orbits of the carbon atoms perpendicular to the chain axis, and, since the diamagnetic susceptibility of a substance in any given direction is proportional to the sum of the squares of the average electronic radii in the plane perpendicular to that direction, it would give rise to a susceptibility parallel to the chain axis larger than that perpendicular to it. Such an effect has been found for polyethylene.[1]

The principal susceptibilities of the rubbers will depend upon two factors. First, the long-chain hydrocarbon skeleton should have an anisotropy comparable to that of polyethylene with the larger susceptibility parallel to the chain axis. Second, the presence of double bonds, especially in a state of resonance, has been found to introduce a diamagnetic anisotropy opposite in sign to that of the saturated hydrocarbons,[11] with the larger diamagnetic susceptibility perpendicular to the plane of the double bonds. In an unsaturated rubber, both of these effects will operate, opposing each other.

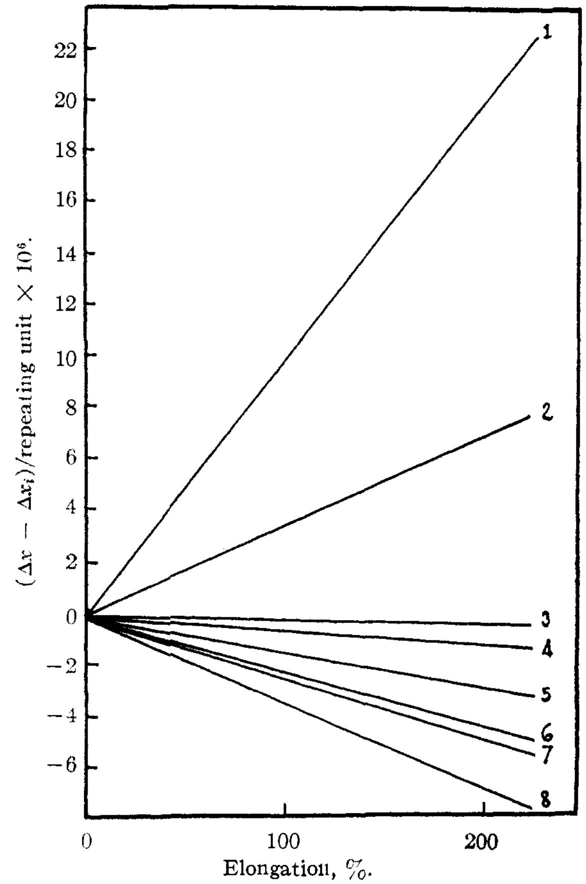

Fig. 2.—Change in magnetic anisotropy of rubber *vs.* per cent. elongation (determined by method of least squares): 1, natural rubber; 2, polybutadiene X-453; 3, polyethylene; 4, polybutadiene XI; 5, Vistanex B-100; 6, Vistanex; 7, butyl rubber; 8, Vistanex B-120.

Natural Rubber and Polybutadiene X-453, both unsaturated, show large increases in anisotropy with stretching, and have the larger principal susceptibility perpendicular to the direction of stretching, and thus perpendicular to the double bonds. The third unsaturated rubber, Polybutadiene VI, has its larger susceptibility parallel to the direction of stretching, but shows only a small change in anisotropy on elongation, the change being almost identical with that of polyethylene.

Natural Rubber shows a greater change in anisotropy with stretching than does Polybutadiene X-453. If the methyl group of the isoprene monomer is magnetically isotropic, the anisotropy of the isoprene and butadiene monomers should be the same, although the principal susceptibilities of isoprene would be larger than those of butadiene. Therefore the difference between the anisotropies of the two rubbers must be due to differences in orientation of the polymers. One possible explanation of such differences in degree of crystallinity is that natural rubber is the *cis*-form of polyisoprene,[12–14] but that polybutadiene is a mixture of *cis*- and *trans*-forms. Thus natural rubber has a regular structure and crystallization can occur easily, but

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[10] C. W. Bunn, "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946, p. 120.

[11] K. Lonsdale, *Proc. Roy. Soc.* (*London*), **A171**, 541 (1939).

[12] C. W. Bunn, *ibid.*, **A180**, 40 (1942).

[13] D. G. Fisher, *Proc. Phys. Soc.* (*London*), **60**, 99 (1948).

[14] R. A. Saunders and D. C. Smith, *J. Applied Physics*, **20**, 953 (1949).

polybutadiene would have an irregular chain and alignment of neighboring chains would be more difficult. Therefore polybutadiene would be more amorphous than natural rubber and would have a smaller anisotropy at any given elongation. However, Field, Woodford and Gehman[15] found that synthetic polyisoprenes probably do not contain any appreciable amount of the *trans*-isomer and it is quite possible that the same is true of polybutadiene.

A more likely explanation can be found on consideration of the work of Kolthoff, Lee and Mairs[16] who analyzed a number of rubbers with perbenzoic acid to find the percentage of "external" double bonds, terminal or side-chain double bonds, as opposed to "internal" ethylenic double bonds within a chain of carbon atoms. It was found that natural rubber has 98.5% of the theoretical unsaturation and no external double bonds, although synthetic emulsion polyisoprene has 99% of the theoretical unsaturation, 13% of this in external double bonds. Emulsion polybutadiene, a 44% conversion polymer, had 99% of the theoretical unsaturation, 22% of which was in external double bonds, while a 75% conversion emulsion polybutadiene had 96% of the theoretical unsaturation and 23% external double bonds. The two polybutadienes considered here, Polybutadiene X-453 and Polybutadiene VI, are 50 and 73% conversion polymers, respectively, and are thus comparable to Kolthoff's two polybutadienes. There must be far more branching in polybutadiene than in natural rubber; on the average there will be one side-chain, formed by 1,2- instead of 1,4-addition, to every three repeating units in the polybutadiene chain. This would decrease the possibility of crystallization on stretching, and the presence of unsaturated side-chains will also increase the smaller principal susceptibility parallel to the chain axis, thus decreasing the anisotropy of the polymer. Probably the actual degree of crystallinity does not affect the anisotropy to any great extent, but rather the possibility of the chain molecules orienting themselves parallel to the direction of stretching is the important factor. Short side-chains will not interfere much with such alignment, but cross-linking will tend to prevent it. The major difference between Natural Rubber and Polybutadiene X-453 is probably the presence of unsaturated side-chains in the latter. These side-chains, if present in the ratio of one to every three repeating units in the chain, would be expected to reduce the anisotropy to about one-half that of an unbranched chain. This is about the observed decrease in anisotropy from Natural Rubber to Polybutadiene X-453, as can be seen from Fig. 2.

Polybutadiene VI appears to be almost amorphous. The number of side-chains appears to be about the same for both 50 and 73% conversion polymers, according to Kolthoff's data. However, there is also a decrease in the per cent. of theoretical unsaturation from 99% in the lower conversion polymer to 96% in the higher conversion one. If this decrease can be attributed solely to cross-linking, there is about one cross-linkage to every twenty chain repeating units in the higher conversion polymer and one cross-linkage for every seventy-five or eighty repeating units in the lower conversion polymer. A high number of cross-linkages in Polybutadiene VI would prevent the molecular chains from aligning themselves parallel to the direction of stretching to any great extent and thus decrease the anisotropy greatly. There is no obvious reason why the principal susceptibility parallel to the direction of stretching should be the larger one.

The four polyisobutylenes, Butyl Rubber and the three Vistanex samples, all have the larger principal susceptibility parallel to the direction of stretching and thus to the extended chain. Since these rubbers are saturated the only contribution to the anisotropy should be that due to the broadening of electronic orbits perpendicular to the chain axis as in polyethylene. However, the principal susceptibility parallel to the chain increases much more with elongation in the polyisobutylenes than in polyethylene. The methyl groups must cause a much greater broadening of the electronic orbits perpendicular to the chain axis than do hydrogen atoms. This must also occur in natural rubber though not to the same extent as in polyisobutylene, since natural rubber has only a quarter as many methyl groups. Even in polybutadiene the side-chains should slightly increase the susceptibility parallel to the direction of stretching, in addition to the effects of unsaturation of the side-groups. Thus in Natural Rubber and in Polybutadiene X-453 the contribution of the double bonds to the principal susceptibility perpendicular to the direction of stretching must be even greater than is apparent from Fig. 2.

Vistanex and Butyl Rubber show an almost identical change in anisotropy with elongation. This indicates that the degree of orientation is the same in both, since the monomer units are the same. Apparently the molecular weight of the polyisobutylene also affects the anisotropy, for the change in anisotropy with elongation is greater in Vistanex B-120 than in Vistanex B-100. Thus there must be a higher degree of orientation in the higher molecular weight polymer. Polyisobutylene shows a very strong crystalline X-ray picture at high elongations[17–19] and apparently the higher molecular weight Vistanex B-120 becomes crystalline at lower elongations than do the other polyisobutylenes. Vistanex lies between the high and low molecular weight polyisobutylenes and probably has a molecular weight somewhere between the two, or at least a wider distribution of molecular weights. At very high elongations all three should approach the same anisotropy change between the unstretched and the highly stretched polymers, and Butyl Rubber should also approach the same limit.

It should be noted that the change in anisotropy of Natural Rubber did not tend toward a limit at the highest elongations used, as reported by Cotton-

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[15] J. E. Field, D. E. Woodford and S. D. Gehman, *J. Applied Physics*, **17**, 386 (1946).

[16] I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, (1947).

[17] C. S. Fuller, *Chem. Revs.*, **26**, 143 (1940).

[18] C. S. Fuller and W. O. Baker, *J. Chem. Ed.*, **20**, 3 (1943).

[19] C. W. Bunn, *J. Chem. Soc.*, 297 (1947).

Feytis.[4] However, she did not find this effect at elongations below 400%, which is greater than any employed here. Since she only reports the period of oscillation in and out of the field for the Krishnan oscillation method, and does not report the actual anisotropies of her rubber samples, it is impossible to tell whether or not her results at lower elongations agree with those found here.

Finally, the change in anisotropy with time, at any one elongation, was found to be small at all elongations, at least for Natural Rubber, and the changes were almost the same for each elongation and therefore would not change the slope of the curve showing the change of anisotropy with elongation.

EVANSTON, ILLINOIS RECEIVED OCTOBER 20, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Entropy of Gold from 15 to 300°K.[1]

BY T. H. GEBALLE AND W. F. GIAUQUE

RECEIVED JANUARY 8, 1952

The heat capacity of single crystal gold has been measured from 15 to 300°K. The heat capacity at constant volume has been calculated and compared with the Debye equation, which is used only as an idealized reference curve. The results, compared with those on several other face centered cubic metal crystals, show that the distribution of vibrational frequencies is characteristic of each metal. This is in agreement with the theoretical expectations of Blackman. The entropy, heat content and free energy have been tabulated. The entropy, less nuclear spin and isotope effects, was found to be 11.32 ± 0.02 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

Some years ago the heat capacities of single crystals of aluminum, copper,[2] silver and lead[3] were measured from 15–300°K. These metals were selected for comparison because they were all face centered cubic structures.

A crystal of gold was prepared at about the same time but heat capacity measurements, which were postponed by the war, were completed only recently. The calorimeter and the procedure for preparing the crystal were the same as those used previously.[2] The temperature scale was in terms of a standard copper–constantan thermocouple, with the laboratory designation W-26, which was originally calibrated against a helium gas thermometer. It was checked against the triple point (13.92°K.) and boiling point (20.36°K.) of hydrogen, and the triple point of nitrogen (63.15°K.) just before the present experiments. The comparison was made in a manner that permitted the simultaneous calibration of the resistance thermometer and thermocouple at the above points.

The gold was obtained from the American Platinum Works, Newark, New Jersey, and was stated to be 99.99% pure. Analyses made by Dr. W. R. Forsythe in this Laboratory showed that silver, copper and iron if present were less than 0.001% each. The crystal investigated had a weight of 2504.12 g. *in vacuo*. The melted gold was solidified over a period of about 12 hours in the apparatus described previously[2] for the preparation of single crystals. The molecular weight was taken as 197.2.

The observed data are given in Table I. One calorie is taken as 4.1840 absolute joules. The runs were made in two series and the observations were continuous in the sense that each run started where the previous one ended. Thus the range was completely investigated. A smooth curve through the data is believed to be accurate to 0.1 to 0.2% above 35°K., at 20°K. the error may be 1%, and at 15° it may be 3% due to decreasing sensitivity of the resistance thermometer.

TABLE I

HEAT CAPACITY OF GOLD, CAL. DEG.$^{-1}$ (G. ATOM)$^{-1}$

Atomic Wt. = 197.2; 0°C. = 273.16°K.

T, °K. Average	C_p	T, °K.	C_p	T, °K.	C_p
Series I		108.65	5.257	253.81	5.970
15.81	0.402	116.89	5.341	263.63	5.992
18.35	.629	125.05	5.411	272.47	6.005
21.16	.873	133.54	5.489	Series II	
24.70	1.210	142.25	5.555	205.46	5.864
29.19	1.672	150.88	5.624	211.14	5.876
34.76	2.226	159.58	5.673	220.50	5.888
40.12	2.687	167.82	5.711	230.01	5.906
45.17	3.072	176.12	5.755	239.82	5.928
50.98	3.470	184.40	5.785	249.95	5.957
57.41	3.848	192.70	5.805	259.68	5.980
63.85	4.145	202.79	5.848	269.96	6.005
70.66	4.406	211.30	5.849	280.20	6.022
78.27	4.650	219.92	5.880	288.41	6.044
85.67	4.835	228.60	5.900	298.46	6.089
93.19	4.984	237.38	5.916	309.02	6.095
100.82	5.132	246.12	5.948		

The heat capacity of gold has been measured by Clusius and Harteck[4] from 15 to 211°K. They do not give the purity or physical state of their gold sample. Over the ranges 15 to 35°K. and 70 to 90°K. their results agree quite well with the present measurements. Between 35 and 70° their results are several per cent. high and from 90 to 211°K. about 1% high. However, the particular calorimeter which they used was not well adapted for observations at temperatures considerably different from that of the bath, an effect which is not uncommon in earlier work. Their results near the temperatures of liquid hydrogen and liquid air are the ones in good agreement.

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(1) This work was supported in part by the Office of Naval Research, United States Navy.

(2) W. F. Giauque and P. F. Meads, THIS JOURNAL, **63**, 1897 (1941).

(3) P. F. Meads, W. R. Forsythe and W. F. Giauque, *ibid.*, **63**, 1902 (1941).

(4) K. Clusius and P. Harteck, *Z. physik. Chem.*, **134**, 243 (1928).