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Pressure Dependence of the Elastic Constants of Beryllium and Beryllium-Copper Alloys*

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The elastic constants of beryllium and of alloys containing 1.1 and 2.4 wt% copper (0.16 and 0.35 at.%) have been measured by a pulse-echo-overlap method. These stiffness coefficients in units of 10^{12} dyn/cm^2 are:

Crystal	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}
Be	2.954	3.561	1.706	0.259	−0.01
Be–1.1% Cu	2.948	3.597	1.702	0.278	⋯
Be–2.4% Cu	2.931	3.552	1.731	0.301	0.03

The effect of hydrostatic pressures up to 6 kbar is indicated by the pressure derivatives given below:

Crystal	dC_{11}/dP	dC_{33}/dP	dC_{44}/dP	dC_{12}/dP	dC_{13}/dP
Be	6.92	8.98	2.55	2.76	3.3
Be–1.1% Cu	7.13	7.79	2.62	2.86	⋯
Be–2.4% Cu	12.01	13.42	2.58	7.73	−2.8

The coefficient $C_{13}=-0.01$ is unusual for a metal; this value indicates that there is no coupling between a tensile stress along the c axis and a resolved stress in the basal plane. This anisotropy in the bonding mechanisms for the two principal directions has been correlated with the band structure and may account for the relatively easy cleavage of beryllium along the basal plane.

I. INTRODUCTION

THIS paper discusses measurements of the elastic constants of zone-refined beryllium crystals and of crystals containing 1.1 and 2.4 wt % copper (0.16 and 0.35 at.%). Beryllium ($1s^22s^2$) has a low atomic weight but it is fairly dense, $\rho=1.85$ g/cm^3, heavier than sodium ($2p^63s^1$), $\rho=0.97$ g/cm^3, or magnesium ($2p^63s^2$), $\rho=1.74$ g/cm^3. The relatively dense packing of beryllium is reflected in its small lattice parameter, $a=2.29$ Å, $c=3.58$ Å; the unit cell has about one-half the volume of a magnesium, zinc, cadmium, or cobalt unit cell. Beryllium has the highest Debye temperature ($\Theta_D=1463°$) and the lowest Poisson's ratio ($\nu=0.02$) of any metal.

The beryllium elastic constants were previously measured by Smith and Arbogast.[1] However, since the acoustic velocities in beryllium (from which elastic properties are determined) are quite high—of the order 7–14 km/sec—it appeared that more accurate values could be obtained by an improved, more precise technique. Elastic properties of alloys of beryllium with small amounts of copper are also of interest because copper is one of the few elements which can dissolve substitutionally in beryllium, and these alloys exhibit slightly higher yields strengths than the pure material.

Pressure derivatives provide insight into the anharmonic properties and serve as parameters in equations of state for solids. Effects of hydrostatic pressures up to 6 kbar were investigated and compared with those for other hexagonal metals. Using the criteria defined by Chung,[2] these pressures are relatively low; the changes with hydrostatic pressure were therefore linear.

Beryllium is an engineering material of high stiffness and low density, but it tends to cleave easily at room temperature. Our measurements of elastic constants indicate that the bonding mechanism in beryllium is anisostropic. Therefore, it is probable that the cleavage properties are primarily an inherent property of beryllium and a consequence of the bonding mechanism.

II. EXPERIMENTAL METHOD

The crystals used in these experiments (prepared by the Franklin Institute, Philadelphia, Pa.) are described in Table I. The pure beryllium crystals were cut from

TABLE I. Beryllium and beryllium-copper crystals.

Sample	Copper (wt %)	(at.%)	x-ray density (g/cm^3)	Orientation	Dimensions (mm)
1	0	0	1.8477	46° to c axis	12.860 ±0.001
					12.95
					12.54
2	0	0	1.8477	(0001)	12.509 ±0.001
				$(10\bar{1}0)$	12.163
				$(11\bar{2}0)$	12.735
3	1.1	0.155	1.8628	(0001)	12.276 ±0.001
				$(10\bar{1}0)$	11.598
				$(11\bar{2}0)$	11.431
4	2.4	0.350	1.8823	(0001)	8.844 ±0.001
				$(10\bar{1}0)$	7.926
				$(11\bar{2}0)$	6.696
5	2.9	0.430	1.8902	44.3° to c axis	6.079 ±0.001
				45° to c axis	6.148
				18° to c axis	12.390

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[1] J. F. Smith and C. L. Arbogast, J. Appl. Phys. 31, 99 (1960).

[2] D. H. Chung, J. Phys. Chem. Solids **29**, 417 (1968).

TABLE II. Velocity and C_{ij} relationship for beryllium.

Mode	Velocity (km/sec)	Elastic constant	Propagation direction (axis)	Particle motion (axis)
V_{l33}	13.833	$(C_{33}/\rho)^{1/2}$	parallel c	parallel c
V_{s44a}	9.609	$(C_{44}/\rho)^{1/2}$	parallel c	normal c
V_{l11}	12.644	$(C_{11}/\rho)^{1/2}$	parallel a	parallel a
V_{s44b}	9.609	$(C_{44}/\rho)^{1/2}$	parallel a	parallel c
V_{s66b}	8.540	$(C_{66}/\rho)^{1/2}=[\frac{1}{2}(C_{11}-C_{12})/\rho]^{1/2}$	parallel a	normal c
V_{ql}		$C_{13}=[2/\sin(2\theta)]\{(C_{11}\sin^2\theta+C_{44}\cos^2\theta-\rho V^2)\times(C_{33}\cos^2\theta+C_{44}\sin^2\theta-\rho V^2)\}^{1/2}-C_{44}$	θ to c	θ to c
V_{ql}'	13.433		46° to c	46° to c

the same zone-refined rod, which had been subjected to 12 refining passes. The alloy crystals were cut from rods which had been alloyed by wrapping copper wire about the pure material and zone-leveling for two passes. Opposite faces of each crystal were ground parallel to ±0.001 mm. Orientations were determined to a precision of ±0.25 deg. The impurity content of the pure beryllium was estimated as 300 ppm from a fluorescent x-ray analysis, with the major contaminants being O, Na, Al, Cl, Fe, Ni, and Co. Copper composition of the highest alloy crystals varied slightly as indicated in Table I. We have reported our results for an average copper content of 2.4 wt %, but it is evident that there were small local variations in composition.

The elastic constants were measured by means of a modification of the pulse-echo-overlap method of Papadakis.[3,4] X and Y cut quartz transducers were used at a 20-MHz carrier frequency. In this technique a short pulse of the carrier is applied to the transducer to initiate an acoustic pulse-echo train in the sample. A pair of successive echoes are intensified and all others suppressed on a cathode-ray oscilloscope tube. The oscilloscope is triggered externally with a variable oscillator so that a cycle-for-cycle match of the two intensified echoes is achieved. When there is a proper match, the triggering frequency is the reciprocal of the delay time between echoes, and the velocity of sound can be determined. This method provides considerably greater accuracy in determining acoustic velocities than techniques which require measurement of delay times directly, especially in cases where the velocities are high.

The effects of hydrostatic pressures were measured in a single stage hydraulic free piston intensifier in which the cylinder bore on the high pressure side of the unit also served as the pressure bomb. The pressure fluid was petroleum ether. Pressure was read to an accuracy of 5 bar on a calibrated Heise gauge. The runs were made to 7.5 kbar at first but were later reduced to 6 kbar to minimize transducer cracking. Transducers were bonded to samples with a polymer made from equal parts of phthalic anhydride and glycerine which is insoluble in the petroleum ether.

The principal sources of error in the elastic constant measurements may be listed as follows:

(1) precision in measuring the sample length,
(2) inaccuracies in the orientation of the crystal,
(3) misorientations of the transducer, and
(4) correction for the phase shift of the bond.

The error in the length measurement, using a micrometer, is about two parts in 10^4. Inaccuracies in the orientation of a crystal of ±0.25 deg will result in an error no greater than two parts in 10^5 for our samples.[5] Errors in the orientation of the transducer in our

TABLE III. Elastic stiffness constants (10^{12} dyn/cm^2).

Material		C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	c/a
Present work	Be	2.954	3.561	1.706	1.348	0.259	−0.01±0.02	1.568
Smith and Arbogast (Ref. 1)	Be	2.923	3.364	1.625	1.328	0.267	0.14	1.568
Schmunk and Smith (Ref. 8)	Mg	0.5974	0.6170	0.1639	0.1680	0.2614	0.217	1.623
Chang and Himmel (Ref. 9)	Cd	1.145	0.5085	0.1985	0.375	0.395	0.399	1.886
Bass *et al.* (Ref. 10)	H_2O (257°K)	0.135	0.145	0.0317	0.035	0.065	0.052	1.629

Elastic compliance coefficients (10^{-12} cm^2/dyn)

Material		S_{11}	S_{33}	S_{44}	S_{12}	S_{13}
Present work	Be	0.3411	0.2808	0.5862	−0.0299	0.001

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[3] E. P. Papadakis, J. Acoust. Soc. Am. **42**, 1045 (1967).

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[5] P. C. Waterman, Phys. Rev. **113**, 1240 (1959).

experiments[6] were on the order of one part in 10^4. The correction of McSkimin and Andreatch[7] for the phase shift of the bond has been used, and we estimate that the error from these sources is also one part in 10^4. Efforts were made to minimize the errors in each case, and we estimate the total experimental error in the elastic constants as four parts in 10^4. The major error in the pressure measurement is in the determination of pressure: We estimate that this was accomplished within 2%.

The acoustic velocities were measured in the principal directions for each crystal. x-ray densities were used in calculating the elastic constants. These velocities are listed in Table II.

III. RESULTS

The adiabatic elastic constants of beryllium at room temperature determined in this investigation are given in Table III and compared with the earlier values of Smith and Arbogast.[1] The two sets of data are in general accord. The most significant difference is in our value $C_{13}=-0.01$, compared with a somewhat higher value in the earlier work. The constant C_{13} is an off-diagonal element of the elastic tensor and is determined from a quasi-pure-mode measurement in a noncrystallographic direction. Our particular values of C_{11}, C_{33}, C_{44}, and C_{66} are involved in the final calculation of C_{13}, and the final value of $C_{13}=-0.01$ is estimated as accurate to ± 0.02. This contrasts with the value $C_{13}=0.14$ in the earlier work.[1] Also listed for purposes of comparison are the corresponding elastic constants for magnesium,[8] cadmium,[9] and hexagonal ice.[10]

Elastic compliances S_{ij} for pure beryllium are also listed in Table III. The values S_{12} and S_{13} are both close to 0, which is consistent with the bulk average of Poisson's ratio, $\nu=0.02$ (listed in Table IV).

Ratios of elastic constants, which indicate anisotropy, are given in Table IV. The coefficient C_{33} corresponds to a longitudinal wave traveling along the c axis, and C_{11} to a longitudinal wave in the basal plane. The two shear constants are C_{44} and C_{66} $[C_{66}=\frac{1}{2}(C_{11}-C_{12})]$. Since the ratios of the shear and longitudinal constants are close to unity, it is evident that beryllium is elastically rather isotropic. We have also computed the bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, using the averaging method described by Voigt.[11] These bulk properties, also listed in Table IV, were calculated from weighted averages of the single-crystal elastic constants using Voigt's assumption that the uniform strain is equivalent to the external strain. Reuss[12] has also provided a method of averaging using the assumption that the uniform stress is equivalent to the external stress. This average for the bulk modulus results in a value $K_{(R)}=1.11$ and $G_{(R)}=1.55$. Differences in the two methods of averaging are quite small in the case of beryllium because of the low elastic anisotropy.

TABLE IV. Anisotropy ratios and bulk elastic properties (10^{12} dyn/cm^2). ν=Poisson's ratio, K_v=bulk modulus (Voigt), G_v=shear modulus, E_v=Young's modulus, C_{ij}=elastic stiffness constants. Cu contents in wt %.

Material		C_{33}/C_{11}	C_{44}/C_{66}	ν	K_v	G_v	E_v
Present work	Be	1.21	1.265	0.02	1.10	1.56	3.18
	Be–1.1% Cu	1.22	1.275	0.02	1.12	1.56	3.20
	Be–2.4% Cu	1.21	1.216	0.03	1.13	1.56	3.20
Smith and Arbogast (Ref. 1)	Be	1.151	1.224	0.05	1.14	1.43	3.12
	Mg	1.032	0.976	0.29	0.352	0.173	0.445
	Cd	1.044	0.529	0.30	0.510	0.240	0.626
	ice	1.074	0.906	0.18	0.103	0.084	0.036

The elastic stiffness constants of the beryllium-copper alloys are summarized in Table V. Relatively small differences were observed on alloying, but this is expected since the alloy content was quite low. Anisotropy ratios and bulk elastic properties for the alloys, which are summarized in Table IV, are also similar to the values for pure beryllium.

Since the intermediate alloy (1.1 wt % copper) was represented by only one sample, we were unable to determine a value of C_{13}; a value of 0.015 was assumed in calculating the bulk properties. Because there was a small difference in the assayed copper concentration (2.4 versus 2.9 wt %) for the two samples of higher alloy content, and because one of the samples was rather small compared to the other, we estimated that the error brackets for C_{13} for this material are twice as large as for pure beryllium.

TABLE V. Elastic stiffness constants of Be-Cu alloys (10^{12} dyn/cm^2). Cu contents in wt %.

Material	Density	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
Be	1.8477	2.954	3.561	1.706	1.348	0.259	-0.01 ± 0.02
Be–1.1% Cu	1.8628	2.948	3.597	1.702	1.335	0.278	···
Be–2.4% Cu	1.8823	2.931	3.552	1.731	1.315	0.301	0.03 ± 0.04

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[12] A. Reuss, Z. Angew. Math. Mech. **9**, 49 (1929).

TABLE VI. Pressure derivatives of elastic constants.

Material	dC_{11}/dP	dC_{33}/dP	dC_{44}/dP	dC_{66}/dP	dC_{12}/dP	dC_{13}/dP
Present work						
Be	6.92±0.03	8.98±0.03	2.55±0.03	2.08±0.03	2.76±0.05	3.3±0.1
Be–1.1% Cu	7.13±0.03	7.79±0.03	2.62±0.03	2.13±0.03	2.86±0.05	···
Be–2.4% Cu	12.01±0.03	13.42+0.03	2.58±0.03	2.14±0.03	7.73±0.05	−2.8±0.1
Schmunk and Smith (Ref. 8)						
Mg	6.11	7.22	1.58	1.36	3.39	2.6
Corll (Ref. 13)						
Cd	9.29	7.26	2.38	2.59	4.10	5.7

Hydrostatic pressure derivatives for both beryllium and the alloy samples are given in Table VI and pressure derivatives of the bulk elastic properties are summarized in Table VII. These values are compared with similar data for magnesium[8] and cadmium.[13] The pressure derivative of Poisson's ratio at $P=0$ is also given in Table VII.

IV. DISCUSSION

A. Elastic Properties of Beryllium

The elastic properties of beryllium are related to the unusual nature of its elastic constant tensor. The off-diagonal elements of the elastic tensor, C_{12} and C_{13}, represent coupling factors between the various pure modes of acoustic propagation in the crystal. The constant C_{12} couples the shear and longitudinal waves polarized and propagating in the basal plane. Although the constant C_{13} does not enter into the acoustic-wave equation for propagation parallel and perpendicular to the *c* axis, it appears in the expression for acoustic velocities for all other orientations. C_{13} is thus a measure of the deviation in the sound velocity for a wave propagating at an angle to the *c* axis from the value obtained by a geometric superposition of waves propagating parallel and perpendicular to the *c* axis. A value of $C_{13}=0$ indicates that there is no coupling between waves propagating in the basal plane and those propagating parallel to the *c* axis. A sound wave traveling at an angle to the *c* axis is simply resolved trigonometrically in these two directions.

The corresponding elastic constants for magnesium,[8] cadmium,[9] and ice,[10] as well as beryllium, are listed in Table III. The pure-mode elastic constants of magnesium and cadmium are much smaller than those of beryllium. It should be noted, however, that the value of the coefficient C_{13} is on the order of the value for C_{12}, and that, in both cases, these are about the same as the shear constants. Beryllium is thus a unique metal, with very large pure-mode elastic coefficients but with very small coupling constants. Hexagonal ice also has a small value for the coefficient C_{13}, but all of its elastic constants are small and of the same order.

TABLE VII. Pressure derivatives of bulk elastic constants.

Material	dK_v/dP	dG_v/dP	$d\nu/dP$ (bar^{-1})
Be	4.60±0.05	2.33±0.05	8×10^{-7}
Be–1.1% Cu	4.55±0.05	2.31±0.05	8×10^{-7}
Be–2.4% Cu	4.63±0.05	3.81±0.05	4×10^{-7}
Mg	4.05±0.05	1.63±0.05	4×10^{-7}
Cd	6.32±0.05	2.16±0.05	4×10^{-7}

B. Effects of Hydrostatic Pressure

The hydrostatic pressure derivatives are compared with those for magnesium[8] and cadmium[13] in Table VI. Despite the rather large differences in the elastic constants of these materials, the pressure derivatives of beryllium, magnesium, and cadmium are quite similar. The effects of adding copper to beryllium are substantial; the pressure derivatives for the alloy containing 2.4 wt % copper are almost twice as large as for the pure material. These differences probably arise from defects in packing associated with the introduction of copper into the lattice.

C. Bonding of Beryllium

We have made an attempt to correlate the apparently unique binding mechanism in beryllium with the electronic energy levels in reciprocal space.

Two band calculations have been made for beryllium: Loucks and Cutler[14] used an orthogonal-plane-wave (OPW) calculation to determine the Fermi surface; Terrell[15] used the augmented-plane-wave (APW) method and obtained rather good agreement with the OPW results. Terrell has also shown how beryllium deviates from free-electron behavior. The calculations of Terrell indicate that some of the wave functions have a *p*-like behavior in beryllium. In contrast, the Fermi surface of magnesium determined from the band-structure calculation of Falicov[16] indicates that magnesium is a free-electron metal. Beryllium is a metal by virtue of the overlap of the atomiclike wave func-

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tions near the Fermi level. It is this overlap which gives the crystalline wave function a significant *p*-like character slightly below and above the Fermi level and which results in deviations from a free-electron model.

One of the striking features of the band structure of beryllium is that the Fermi level does not intersect any energy levels for a slice perpendicular to the basal plane and coplanar with the *c* axis. There is also no intersection of energy levels with the Fermi surface for a basal-plane slice of the Brillouin zone close to an edge of the zone. The basal-plane slice in the center of the Brillouin zone has a Fermi level cutting through a number of bands, providing the major contribution to the electronic specific heat.

In an extended zone scheme the band structure is such that the electrons overlap along the basal plane, but there is no overlap in the *c* and $[10\bar{1}0]$ directions in the first two Brillouin zones. The bonding is therefore anisotropic, and the bonding interaction between atoms lying in the basal plane is different from the interaction between atoms along the *c* axis. Although the charge distribution in real space has not been calculated, it is not spherically symmetric, and is considerably different in the two principal directions. This situation is quite consistent with the observation of a lack of coupling between the force systems parallel and perpendicular to the *c* axis. When a correlation between values of Poisson's ratio and the plastic properties of hexagonal metals was made some years ago, Pugh[17,18] came to somewhat similar conclusions.

V. CONCLUSIONS

The pure-mode elastic constants of beryllium were unusually high, indicating a high resistance to elastic deformation. A unique type of lattice dynamics was indicated for beryllium by the values $C_{13}=-0.01$ and Poisson's ratio $\nu=0.02$. Beryllium appears to behave as if it could be described by two interpenetrating force systems, one which responds to acoustic waves propagating in the basal plane, and one which responds to acoustic waves propagating parallel to the *c* axis. This anisotropic bonding mechanism was common to crystals of all compositions tested. No significant trends in the elastic constants were observed on alloying beryllium with 1.1 and 2.4 wt % copper. Nevertheless, beryllium and its dilute alloys are almost elastically isotropic.

A correlation of the band-structure determinations with the observed properties indicates a charge-density anisotropy which is associated with different binding mechanisms for atoms in the basal plane and atoms along the *c* axis.

Hydrostatic pressure derivatives for the pure material are in line with those for all other materials investigated in this manner. The beryllium-copper alloys show a trend toward an increase in the pressure derivatives of the longitudinal elastic constants with composition, while the shear-mode derivatives do not show any significant change. The sharp increase in the derivatives of the longitudinal elastic constants with copper concentration is attributed to the substitutional occupation of lattice sites by copper atoms.

The brittleness of beryllium may well be a consequence of the unusual lattice dynamics and of the nature of the interatomic bonds along the *c* axis. Since a normal stress component along the *c* axis does not have a mechanism for stress transfer for directions in the basal plane, planes normal to the *c* axis may separate as a result of the stress concentrations introduced by localized plastic flow on the basal plane. The basal cleavage is apparently further enhanced by the bonding along the *c* axis. These bonds, which seem to possess significant covalent-type character, are directed bonds which can suffer little stretching before fracture. The low value of Poisson's ratio implies that cleavage along the basal plane will be favored by such a stress system, resulting in a rather brittle material.

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