necessary for the creation of traps, their exact nature is still unknown.

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# Elastic Constants of Magnesium from 4.2°K to 300°K*

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The adiabatic elastic constants of magnesium single crystals have been measured by an ultrasonic pulse technique. The values at 298°K are in good agreement with the recent values of Long and Smith. The values extrapolated to 0°K are $c_{11}=0.635$, $c_{33}=0.664$, $c_{44}=0.1842$, $c_{12}=0.259$, $c_{13}=0.217$ in units of $10^{12}$ dynes/cm². A Debye characteristic temperature, $\theta$, of 388±3°K has been calculated at 0°K by averaging the inverse cube of the longitudinal and transverse elastic wave velocities over all directions of propagation. Atomic force constants for a central-force model with an electron gas term are also obtained.

## I. INTRODUCTION AND METHOD

THE adiabatic elastic constants of single crystals of the metallic elements at 0°K are of interest in the application of the Born-von Kármán theory of lattice dynamics to metals.[1,2] It has been proposed by de Launay[1] that the deviations from the Cauchy relations which are observed experimentally may arise from an electron gas contribution to the elasticity. If this is the case, a central-force model for the lattice forces may be valid for some metals. For such a central-force lattice model, it is possible to compute the interatomic force constants for a reasonable number of neighbor interactions directly from the elastic constants. Moreover, the low-temperature elastic constants provide an experimental test of the validity of any force model.

Magnesium has a hexagonal close-packed structure with an axial ratio ($c/a$) of 1.623, closely approximating the ratio of 1.633 for ideal closest packing. A crystal with hexagonal symmetry has five independent elastic constants, $c_{11}$, $c_{33}$, $c_{44}$, $c_{66}$ (or $c_{12}$), and $c_{13}$, which can be obtained from the velocity of longitudinal and transverse waves propagating in directions parallel, perpendicular, and at 45° to the $c$ axis. The relations between the elastic constants and acoustical wave velocities ($U$) have been derived previously[2] and are given below.

1. Propagation parallel to the $c$ axis:

$$\rho U_l^2 = c_{33},$$
$$\rho U_t^2 = c_{44} \text{ (any polarization).}$$

2. Propagation perpendicular to the $c$ axis:

$$\rho U_l^2 = c_{11},$$
$$\rho U_t^2 = c_{44} \text{ (polarized parallel to the } c \text{ axis),}$$
$$\rho U_t'^2 = c_{66} = \tfrac{1}{2}(c_{11}-c_{12}) \text{ (polarized perpendicular to the } c \text{ axis).}$$

3. Propagation at 45° to the $c$ axis:

$$\rho U_t^2 = \tfrac{1}{2}(c_{66}+c_{44}) \text{ (polarized perpendicular to the } c \text{ axis),}$$
$$\rho U^2 = \tfrac{1}{4}\{c_{11}+c_{33}+2c_{44} \pm [(c_{11}-c_{33})^2 + 4(c_{13}+c_{44})^2]^{\frac{1}{2}}\}$$
($U_{ql}$ is given by the plus sign; $U_{qt}$, by the minus sign).

The subscripts $l$ and $t$ refer to the longitudinal or transverse character of the wave, and $\rho$ is the density. In the direction at 45° to the $c$ axis, it is possible to propagate only one pure wave (the transverse wave polarized perpendicular to the $c$ axis); the two waves of mixed character obtained in that direction are referred to as quasi-longitudinal ($ql$) and quasi-transverse ($qt$). For magnesium the coupling between these waves is weak, and it is possible to excite only the quasi-longitudinal or only the quasi-transverse waves separately.

In this work the velocity of the pure transverse wave in the direction at 45° to the $c$ axis was measured as a check only at 77.6°K and 298°K. The velocities of the other seven waves enumerated above were measured as a function of temperature from 4.2°K to 300°K and

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[1] J. de Launay, J. Chem. Phys. **21**, 1975 (1953).

[2] L. J. Slutsky and C. W. Garland, J. Chem. Phys. **26**, 787 (1957).

used to calculate the five independent elastic constants of magnesium.

## II. EXPERIMENTAL

A single crystal of magnesium grown in the form of a cylinder 2 inches in diameter and 4 inches long was obtained from Horizons Incorporated.[3] The purity, as determined by the manufacturer, was 99.9+%. Crystal orientation was determined by back-reflection Laue photography, and two samples were machined from the original crystal. One had pairs of parallel faces perpendicular and parallel to the $c$ axis; the other had a pair of parallel faces whose normal was at 45° to the $c$ axis. The fly-cutting operation used in preparing these plane faces introduced serious crystal dislocation to a depth estimated as 0.1 mm, and a layer of disturbed material was removed by polishing with grades of emery paper down to 000, then with aluminum oxide abrasive, followed by etching with dilute acetic acid. Polishing was continued until sharp, round Laue spots were obtained. After polishing, the faces were found to be plane and parallel within 0.001 inch.

With a crystal mounted so that the sixfold Laue symmetry was obtained, the settings on the goniometer were slightly altered and a series of Laue pictures taken. It was found that a difference of 15′ of arc in the goniometer settings produced a distinguishable asymmetry in the photographs. A consideration of the possible errors in camera geometry and the precision with which the various machining operations were carried out establishes 30′ as the probable error in the orientation of the faces and thus in the direction of propagation of ultrasonic waves. These orientation errors may be neglected with respect to the uncertainty in the velocity measurements.

The ultrasonic pulse technique has been described by Huntington.[4] A Du Mont A/R 256-D oscilloscope triggers a pulse oscillator which applies a 10-Mc pulse (approximately 2 $\mu$sec in duration) to a quartz piezoelectric crystal cemented to the sample. The elastic wave so generated travels the length of the sample, reflects off the far end, and on returning is partially reconverted into an electrical impulse by the transducer, which now acts as a receiver. The interval between successive echoes gives directly the transit time of the pulse in the sample. In this work the suggestions made by Overton and Gaffney[5] in regard to calibrating the scope and ranging the echoes were used throughout.

The magnesium sample is enclosed in a small cylindrical copper can, the cover of which makes the rf connection to the quartz transducer. Electrical contact is ensured throughout the temperature range by means of a stainless steel spring between the sample and the bottom of the sample holder.

For measurements in the temperature range 77–300°K, a gas cryostat of the type described by Swenson[6] was used. The sample holder fitted tightly into a copper heat exchanger soldered to the bottom of a stainless steel well, the whole assembly being encased in a vacuum jacket. Cold nitrogen gas flows down through the coils of the heat exchanger and up through the sample case. The temperature is controlled by adjusting the nitrogen flow rate to balance the heat leak by conduction down the well against the heat loss to the circulating nitrogen. Measurements at 77.6°K were made with the sample completely immersed in liquid nitrogen.

A simpler cryostat was used with liquid helium. The sample holder was suspended by cords in a helium Dewar which was immersed in liquid nitrogen. The helium Dewar was filled until the liquid helium level was several inches above the top of the sample holder, and readings were taken at 4.2°K. Subsequent readings were taken as the sample warmed up after the level of liquid helium had fallen below the bottom of the sample holder.

The temperature was measured with a copper-constantan thermocouple cemented or taped directly to the sample. Above 80°K, the temperatures were obtained from the measured emf's and Aston's tables.[7] Below 80°K, a set of corrections were applied to Aston's tables as given by Stephenson[8] for this Leeds and Northrup thermocouple wire. The sensitivity of the thermocouple falls off with decreasing temperature. Above 80°K the temperature can be regarded as accurate to ±0.05°K; below 40°K, ±0.2°K is probably an appropriate assignment of the error in the temperature. No attempt was made to take readings between 4.2°K and 15°K because of the rapid warmup and poor thermocouple sensitivity in this region.

In pulsed ultrasonic measurements it is necessary to have some sort of adhesive seal between the quartz transducer and the sample. Phenyl salicylate (Salol) was found to be suitable in the temperature range 260–300°K. Ice is a good acoustic seal covering the range 200–273°K. Below 200°K a high viscosity silicone fluid[9] (Dow Corning 200) was best. The delays determined directly in this experiment represent the transit time of pulses in the magnesium sample plus the time required for a round-trip transit in the seal. Thus, a correction should be made for the delay in the seal; however, these corrections are small, being of the order of the experimental error, and are difficult to evaluate exactly.

Long and Smith,[10] using Salol as the acoustic seal,

[3] Horizons Incorporated, 2891 East 79th Street, Cleveland 4, Ohio.
[4] H. B. Huntington, Phys. Rev. **72**, 321 (1947).
[5] W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1953).
[6] C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608 (1954).
[7] Aston, Willihnganz, and Messerly, J. Am. Chem. Soc. **57**, 1642 (1935).
[8] C. C. Stephenson (private communication).
[9] We wish to thank the Dow Corning Corporation for providing a sample of silicone fluid with a viscosity of $2.5\times10^6$ centistokes (at 25°C).
[10] T. R. Long and C. S. Smith, Acta Metallurgica **5**, 200 (1957).

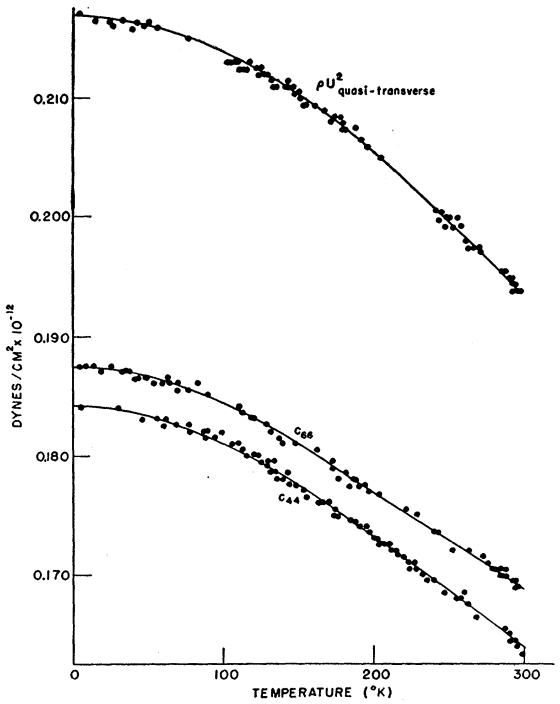


FIG. 1. The adiabatic elastic constants $c_{44}$ and $c_{66}$ and $\rho U^2$ for the quasi-transverse wave in the direction at 45° to the $c$ axis *versus* temperature.

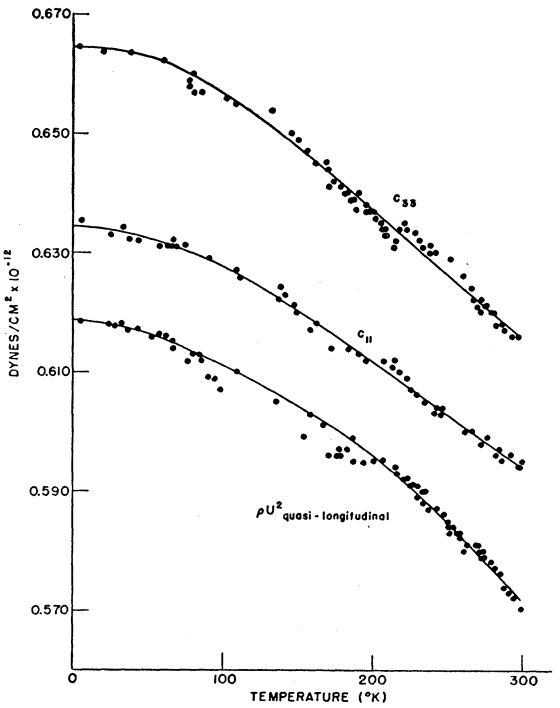


FIG. 2. The adiabatic elastic constants $c_{11}$ and $c_{33}$ and $\rho U^2$ for the quasi-longitudinal wave in the direction at 45° to the $c$ axis *versus* temperature.

have measured the delay of 10-Mc pulses as a function of path length in a magnesium single crystal. They obtained seal corrections of 0.15 $\mu$sec for longitudinal waves and 0.14 $\mu$sec for transverse waves from the slope of a plot of the reciprocal apparent velocity *versus* the reciprocal path length. Overton and Gaffney,[5] applying a similar technique to their measurements on copper, have arrived at a transit time correction of 0.01 to 0.02 $\mu$sec; while Neighbours, Bratten, and Smith[11] have determined corrections of 0.06 to 0.10 $\mu$sec in their measurements on nickel.

The round-trip transit times of 10-Mc pulses in polycrystalline magnesium rods of various lengths (1.2–8.4 cm) were measured to obtain a $(1/U_{app})$ *versus* $(1/L)$ plot, which is virtually horizontal and corresponds to a seal correction of $0.00\pm0.04$ $\mu$sec. The apparatus is poorly suited to the determination of delays less than 5 $\mu$sec, and it is doubtful that an accurate value of the correction could be obtained by this technique. Therefore, the less sophisticated approach of measuring the velocity of sound in Salol at 273°K and the thickness of the Salol seal was used to obtain a seal correction of 0.03 $\mu$sec for longitudinal and 0.04 $\mu$sec for transverse waves. Velocity measurements at 273°K were compared using both ice and Salol, as were measurements at 77°K using ice and silicone, and identical seal corrections were obtained. Overton and Gaffney[5] have stated that seal corrections determined at one temperature are likely to be erroneous. However, constant corrections of 0.03 $\mu$sec and 0.04 $\mu$sec were applied to all our data. A probable error of $\pm0.03$ $\mu$sec in the true transit time in the sample was attributed to the uncertainty in the seal correction.

The path lengths at 20°C were 7.6302 cm parallel to the $c$ axis, 7.5794 cm perpendicular to the $c$ axis, and 9.8623 cm along the direction at 45° to the $c$ axis. A density of 1.7486 g/cm³ at 20°C was calculated from the 1946 atomic weight of magnesium and the lattice parameters determined by Hume-Rothery and Raynor.[12] Changes in the path lengths and the density with temperature were calculated from the data of Goens and Schmid,[13] who have measured the coefficients of thermal expansion of single crystals of magnesium both parallel and perpendicular to the $c$ axis from 20°K to 373°K. It was assumed that the coefficient for thermal expansion for the 45° direction was the average of the parallel and perpendicular coefficients. The total effect on the elastic constants when changes in density and path length are taken into account is less than 1%. Since Goens and Schmid's determinations are unlikely to be in error by as much as 10%, it would appear that the errors in path length and density may be neglected.

The principal source of uncertainty is the accuracy

[11] Neighbours, Bratten, and Smith, J. Appl. Phys. **23**, 389 (1952).

[12] W. Hume-Rothery and G. V. Raynor, J. Inst. Metals **65**, 379 (1939).

[13] E. Goens and E. Schmid, Physik. Z. **37**, 385 (1936).

with which the individual echo pulses may be ranged. The average deviation among the time intervals between successive echo pulses was about ±0.25%. When this error is combined with the uncertainty in the seal correction a probable error of ±0.7% in the directly measured elastic constants is obtained. Simple propagation of errors treatment gives a probable error of 1.8% in the calculated quantities $c_{12}$ and $c_{13}$.

## III. RESULTS

The adiabatic elastic constants of magnesium obtained directly from velocity measurements ($c_{11}$, $c_{33}$, $c_{44}$, $c_{66}$) and those whose calculation requires a knowledge of the other constants ($c_{12}$, $c_{13}$) are plotted in Figs. 1, 2, and 3, along with the values of $\rho U^2$ for the quasi-transverse and quasi-longitudinal waves in a direction at 45° to the $c$ axis. The constants $c_{66}$ and $c_{12}$ are not independent, since $c_{12}$ is calculated from the relation $c_{66}=\frac{1}{2}(c_{11}-c_{12})$. To achieve the best accuracy, values of $c_{13}$ were calculated from the difference of $\rho U^2$ for the quasi-longitudinal and quasi-transverse waves in the 45° direction. Experimental points are shown in Figs. 1 and 3; in Fig. 3 calculated points are not included.

The values of $c_{44}$ obtained from propagation of transverse waves parallel and perpendicular to the $c$ axis agree well within experimental error, as do the values of $c_{33}$ checked by using the sum of $\rho U^2$ for the quasi-transverse and quasi-longitudinal waves in the 45° direction and the measured values of $c_{11}$ and $c_{44}$. Since velocities of only seven different waves were measured throughout the temperature range to determine five elastic constants, these are the only two independent checks possible on the internal consistency of our data.

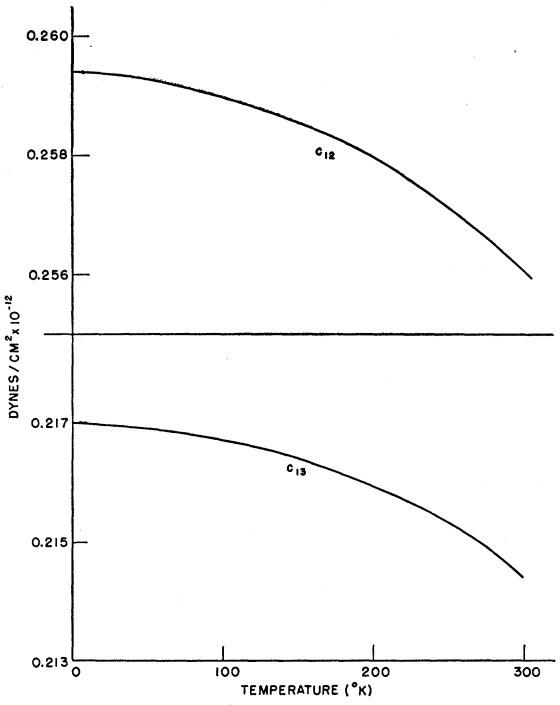


FIG. 3. The adiabatic elastic constants $c_{12}$ and $c_{13}$ *versus* temperature. These quantities are not obtained directly from a single velocity measurement.

TABLE I. The adiabatic elastic constants, $c_{ij}$, and the reciprocal adiabatic compressibility, $K=(2c_{11}+c_{33}+2c_{12}+4c_{13})/9$. All entries are given in units of $10^{12}$ dynes/cm². These values are taken from smooth curves and the number of significant figures does not indicate the accuracy of the absolute value.

| $T$(°K) | $c_{11}$ | $c_{33}$ | $c_{44}$ | $c_{66}$ | $c_{12}$ | $c_{13}$ | $K$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.6348 | 0.6645 | 0.1842 | 0.1875 | 0.2594 | 0.2170 | 0.3689 |
| 20 | 0.6340 | 0.6640 | 0.1840 | 0.1872 | 0.2594 | 0.2170 | 0.3688 |
| 40 | 0.6330 | 0.6635 | 0.1835 | 0.1869 | 0.2593 | 0.2169 | 0.3684 |
| 60 | 0.6315 | 0.6616 | 0.1829 | 0.1862 | 0.2592 | 0.2169 | 0.3676 |
| 80 | 0.6300 | 0.6595 | 0.1820 | 0.1858 | 0.2591 | 0.2168 | 0.3669 |
| 100 | 0.6275 | 0.6566 | 0.1810 | 0.1844 | 0.2590 | 0.2167 | 0.3659 |
| 120 | 0.6249 | 0.6534 | 0.1798 | 0.1830 | 0.2588 | 0.2166 | 0.3650 |
| 140 | 0.6219 | 0.6495 | 0.1783 | 0.1818 | 0.2586 | 0.2165 | 0.3638 |
| 160 | 0.6189 | 0.6455 | 0.1768 | 0.1801 | 0.2585 | 0.2163 | 0.3630 |
| 180 | 0.6154 | 0.6411 | 0.1750 | 0.1785 | 0.2582 | 0.2162 | 0.3614 |
| 200 | 0.6118 | 0.6370 | 0.1732 | 0.1769 | 0.2580 | 0.2160 | 0.3603 |
| 220 | 0.6084 | 0.6326 | 0.1715 | 0.1752 | 0.2576 | 0.2157 | 0.3590 |
| 240 | 0.6049 | 0.6281 | 0.1697 | 0.1738 | 0.2573 | 0.2155 | 0.3574 |
| 260 | 0.6011 | 0.6243 | 0.1678 | 0.1720 | 0.2569 | 0.2152 | 0.3556 |
| 280 | 0.5974 | 0.6200 | 0.1659 | 0.1705 | 0.2565 | 0.2148 | 0.3537 |
| 300 | 0.5940 | 0.6160 | 0.1640 | 0.1690 | 0.2561 | 0.2144 | 0.3524 |

The elastic constants read from smooth curves are tabulated at twenty degree intervals from 0°K to 300°K in Table I. The results of this work are compared with other determinations[10,13–15] of the room-temperature elastic constants of magnesium in Table II. Our results at 298°K are seen to be in good agreement with those recently reported by Long and Smith,[10] who also used an ultrasonic pulse technique.

The reciprocal adiabatic compressibility, $K=(2c_{11}+c_{33}+2c_{12}+4c_{13})/9$, as calculated from the smooth-curve values of the elastic constants, is also given in Table I.

## IV. DISCUSSION

Magnesium resembles the other metals for which low-temperature elastic data are available in that the percentage variation in the shear constants $c_{44}$ and $c_{66}$

TABLE II. The elastic constants of magnesium single crystals at room temperature obtained from the present measurements (P) compared with values obtained by Long and Smith[a] (LS), Bridgman[b] (B), and Goens and Schmid[c,d] (GS). All results are given in units of $10^{12}$ dynes/cm².

| Obs | Temp. | $c_{11}$ | $c_{33}$ | $c_{44}$ | $c_{66}$ | $c_{12}$ | $c_{13}$ |
|---|---|---|---|---|---|---|---|
| P | 298°K | 0.5943 | 0.6164 | 0.1642 | 0.1691 | 0.256 | 0.214 |
| LS | 298°K | 0.5974 | 0.617 | 0.1639 | 0.1675 | 0.2624 | 0.217 |
| B | room | 0.594 | 0.594 | 0.114 | 0.196 | 0.203 | 0.203 |
| GS | 293°K | 0.585 | 0.610 | 0.166 | 0.167 | 0.250 | 0.208 |
| P | 293°K | 0.5952 | 0.6174 | 0.1647 | 0.1695 | 0.256 | 0.214 |

[a] See reference 10.
[b] See reference 14.
[c] See reference 13.
[d] See reference 15.

[14] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **67**, 29 (1932).
[15] E. Goens and E. Schmid, Naturwiss. **19**, 376 (1931).

TABLE III. Lattice force constants ($\alpha$, $\beta$, and $\gamma$, in units of $10^3$ dynes/cm) and the electron gas bulk modulus ($\sigma$, in units of $10^{12}$ dynes/cm$^2$) for magnesium at 0°K and 300°K. As a check on these parameters the calculated value of $c_{11}$ is given together with the experimental value (both in units of $10^{12}$ dynes/cm$^2$).

| $T$(°K) | $\alpha$ | $\beta$ | $\gamma$ | $\sigma$ | $c_{11}$(calc) | $c_{11}$(exp) |
|---|---|---|---|---|---|---|
| 0 | 10.59 | 10.53 | 0.316 | 0.0328 | 0.624 | 0.635 |
| 300 | 9.69 | 9.78 | 0.234 | 0.0498 | 0.585 | 0.594 |

from 0°K to 300°K is about 60% greater than the percentage variation in the compressional constants $c_{11}$ and $c_{33}$. Magnesium is very nearly elastically isotropic; the values of the ratios $c_{66}/c_{44}$ and $c_{33}/c_{11}$ are, respectively, 1.018 and 1.047 at 0°K, and 1.030 and 1.037 at 300°K.

A central-force model for hexagonal close-packed lattices has been described elsewhere.[2] This model involves the interatomic force constants between first ($\beta$), second ($\alpha$), and third ($\gamma$) nearest neighbors plus an isotropic volume-dependent term ($\sigma$) interpreted as the bulk modulus of the conduction electron gas which is obtained from the deviation from the Cauchy relation, $c_{13}=c_{44}$. Values of the force constants (in dynes/cm) and $\sigma$ (in dynes/cm$^2$) for magnesium at 0°K and 300°K are given in Table III. The values were calculated from the experimental values of $c_{33}$, $c_{44}$, $c_{66}$, and $c_{13}$, leaving $c_{11}$ as a check. The values of $c_{11}$ calculated from these force constants and the experimental values are also given in Table III for comparison. In magnesium, which has an axial ratio slightly less than the ideal value, the first and third nearest neighbors of an atom lie in planes above and below the hexagonal net in which the reference atom lies. The second nearest neighbors are in the same net as the reference atom. The first neighbor distance at 0°K is 3.173 A; the second neighbor distance, 3.187 A; and the third, 4.497 A. The near equality of the first- and second-neighbor force constants and the much smaller value of the third-neighbor force constant is thus expected.

Solutions to the lattice dynamical secular equation for magnesium at low temperature (using the 0°K force constants) are now in progress to obtain the frequency spectrum.

In order to evaluate the Debye characteristic temperature, $\theta$, for an anisotropic substance at 0°K it is necessary to average the inverse cube of the elastic wave velocities over all directions of propagation. In magnesium the wave velocities have cylindrical symmetry about the $c$ axis. It is possible to propagate one pure transverse wave in any arbitrary direction and the inverse cube velocity for this branch may be evaluated readily to give

$$\langle 1/U_t^3\rangle_{\text{Av}}=\rho^{\frac{3}{2}}/(c_{44}^{\frac{1}{2}}c_{66}).$$

The averaging for the quasi-longitudinal and quasi-transverse waves may be done graphically or by a series expansion; both give the same result. The Debye characteristic temperature at 0°K calculated from the elastic constants is 388°±3°K. The low-temperature specific heat of magnesium has been measured recently by Smith[16] from 1°K to 20°K on a sample of unspecified purity and by Logan, Clement, and Jeffers[17] from 3°K to 13°K on samples that were 99.95+% Mg with known impurities. The two sets of data agree well over the entire temperature range. Smith, using his data in the range from 1°K to 4°K, reports a $\theta$ value of 406° ±10°K. Logan, Clement, and Jeffers give a $\theta$ value of 390°K based on their data in the region from 3°K to 10°K.

## ACKNOWLEDGMENT

We wish to express our thanks to Professor D. P. Shoemaker, Department of Chemistry, Massachusetts Institute of Technology, for advice and assistance in carrying out the x-ray orientation of the samples.

[16] P. L. Smith, Phil. Mag. 46, 744 (1955).
[17] Logan, Clement, and Jeffers, Phys. Rev. 105, 1435 (1957).