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Debye temperatures of selected silicate minerals

by

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ABSTRACT

The *acoustic* Debye temperatures, Θ_D^e, for 31 silicate minerals have been calculated from their elastic stiffness (c_{ij}'s) constants and/or their heat capacities at very low temperatures. Calculation of the Θ_D^e values from the c_{ij}s' were done on a Hewlett-Parkard series 200 computer using a program written in Hewlett-Packard BASIC.

For those silicates having no magnetic or electronic contributions to their heat capacity for which modern heat capacity measurements below 20 K exist, the calorimetric Debye temperatures, Θ_D^c, are in good agreement with Θ_D^e values obtained from the elastic constants.

INTRODUCTION

Debye's (1912) theory for the heat capacity of a solid provides a simple one parameter model which correctly describes the temperature dependence of C_V at low temperatures. It is based upon a model for the frequency spectrum, $G(\nu)$, of a solid whose significant features are a cutoff or maximum frequency ν_{max}, a total of $3N_A$ frequencies where N_A is Avogadros constant, and a quadratic variation of the number of frequencies (i.e., $dn/d\nu \sim \nu^2$) at low frequency. Debye's model spectrum is given by (e.g. Zemansky, 1968)

$$G(\nu) = (9N_A/\nu_{max}^3)\nu^2 \quad (1)$$

The Debye temperature, Θ_D^e, is directly related to this maximum frequency by

$$\Theta_D^e = (h/k)\nu_{max} \quad (2)$$

or, to the mean velocity of sound in the crystal by

$$\Theta_D^e = (h/k)[3N\rho/4\pi M]^{1/3} v_m \quad (3)$$

where h is Planck's constant = 6.626076×10^{-34} J·s, k is the Boltzman constant = 1.38066×10^{-23} J·K^{-1}, Avogadros constant, $N_A = 6.0221367 \times 10^{23}$ mol^{-1}, ρ is the density, M the formula weight, and v_m is the mean velocity of sound.

Because of the simplicity of the theory and its considerable success in calculating the heat capacity at low temperatures, the concept of a characteristic or Debye temperature has become a central concept in the equation of state of solids. Thus the Debye temperature enters into the Grüneisen theory of thermal expansion, the Lindemann melting relation, and as pointed out by Anderson (1965), given the Debye temperature one may estimate fairly closely the velocity of shear waves in a solid from the approximate relation

$$v_s \approx (\Theta_D/280)(M/q\rho)^{1/3} \text{ km sec}^{-1} \tag{4}$$

where q is the number of atoms in the chemical formula. Thus values for the Debye temperature are of some use to the geophysicist trying to model the thermal parameters of mantle minerals.

Θ_D FROM $C_p^o(T)$ MEASUREMENTS

At sufficiently low temperatures the vibrational spectrum of a solid is composed of frequencies in the "acoustic" range (i.e., $5\text{x}10^{13}\text{sec}^{-1}$ or less), optical frequencies are not excited and the heat capacity is given by (e.g., Slater, 1939)

$$C = \frac{12R\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3 = 1943.8\left(\frac{T}{\Theta_D}\right)^3 \tag{5}$$

where $R=N_A \cdot k$ is the gas constant, = 8.31451(7) $J \cdot mol^{-1} \cdot K^{-1}$, T is the Kelvin temperature, and $C = C_v \approx C_p^o$. Thus C will vary as T^3 and a plot of C/T against T^2 will be a straight line passing through the origin. One may therefore obtain a purely acoustical value for the Debye temperature (Θ_D^C) from heat capacity measurements at low temperatures using (5). We stress that equation (5) is valid only for temperatures of the order of $T < \Theta_D/50$. This is shown in Figure 1 where we have plotted the C_p^o measurements of Krupka et al. (1985) for synthetic enstatite and wollastonite, and those of Hemingway et al. (1986) for phenakite.

Equation (3) and (5) are applicable to monoatomic solids only. For a polyatomic solid one must multiply (3) by $q^{1/3}$ and (5) by q.

Θ_D FROM ELASTIC CONSTANTS

One may also obtain a (purely acoustical) value for Θ_D from the mean velocity of sound in a crystal from equation (3). The difficulty in calculating a mean sound velocity in a low-symmetry crystal arises from the complex variation of v with direction as shown in Figure 2. For any direction in a crystal the velocity of sound can be calculated from the elastic stiffness constants and the density of the crystal by using the Christoffel equation

$$\begin{vmatrix} \Gamma_{11}-\rho v^2 & \Gamma_{12} & \Gamma_{13} \\ \Gamma_{12} & \Gamma_{22}-\rho v^2 & \Gamma_{23} \\ \Gamma_{13} & \Gamma_{23} & \Gamma_{33}-\rho v^2 \end{vmatrix} = 0, \qquad (6)$$

which is a cubic in ρv^2. The Γ_{ij} are complex functions of the elastic constants and of the direction cosines of the propogation direction of the sound wave. For any direction in the crystal there will be three solutions to this equation corresponding to the two shear (transverse) velocities and one longitudinal (compressional) velocity. By solving the Christoffel equation for various directions one may, by a numerical integration procedure, obtain the mean sound velocity. The calculational procedures are discussed in detail by Robie and Edwards (1966). Thus if we have values for the c_{ij} for a crystal, we can obtain a purely acoustical value for the Debye temperature. To this end, the procedure described by Robie and Edwards (1966) was programmed in Hewlett-Packard BASIC for a personal computer. A listing of this program is given in the Appendix.

The development of the Brillouin scattering technique for measuring the velocity of sound in microcrystals by Weidner et al. (1975) together with the velocity inversion procedure to obtain the elastic stiffness constants by Weidner and Carleton (1977) was a major experimental advance and in recent years has provided accurate elastic constant data for a number of low-symmetry silicate minerals.

Because of the usefulness of the Debye model for extrapolating measured C_p^o data to zero kelvin, we have collected the more recent elastic constant data for silicate minerals and used these data to calculate Debye temperatures. To be strictly rigorous one should compare the Θ_D values obtained from low-temperature heat capacity data with Θ_D calculated from elastic constants *also* measured at low temperatures. The temperature variation of the elastic constants is usually fairly small and can normally be neglected. As an example the Debye temperatures of forsterite calculated from the elastic constants of Sumino et al. (1977) measured at 83 and 293 K are 767 and 757 K respectively.

The results of these calculations together with the source of the elastic constants are listed in Table 1. Where available, we have also tabulated values for Θ_D^c calculated from low temperature heat capacity data in the temperature range $T < \Theta/25$.

Table 1. Debye temperatures of some silicate minerals calculated from their elastic stiffness constants or from low-temperature heat capacities.

Name and formula	Density	v_m	Θ_D^e	Θ_D^c	Source
	$g \cdot cm^{-3}$	$km \cdot sec^{-1}$	K	K	
Coesite SiO_2	2.911	5.042	666		Weidner and Carleton (1977)
Stishovite SiO_2	4.290	7.864	1183		Weidner, Bass Ringwood and Sinclair (1982)
Kyanite Al_2SiO_5	3.675			1100	Robie and Hemingway (1984)
Andalusite Al_2SiO_5	3.145	6.204	838	855	Vaughan and Weidner (1978) Robie and Hemingway (1984)
Phenakite Be_2SiO_4	2.960	6.473	933	939	Yeganek-Haeri and Weidner (1985) Hemingway et al. (1986)
Beryl $Be_3Al_2(Si_6O_{18})$	2.698	6.043	799		Yoon and Newnham (1973)
Tourmaline (uvite) $CaMg_3(MgAl_5)BSi_6O_{30}(OH,F)$	3.061	5.673	770		Tatli (1985)
Sillimanite Al_2SiO_5	3.241	5.927	809	730	Vaughan and Weidman (1978) Robie and Hemingway (1984)
Grossular $Ca_3Al_2Si_3O_{12}$	3.595	5.981	816		Halleck (1973)
Uvarovite $Ca_3Cr_2Si_3O_{12}$	3.850	5.440	733		Bass (1986)
Andradite $Ca_3Fe_2Si_3O_{12}$	3.836	5.386	721		Bass (1986)

Table 1 (page 2)

Name and formula	Density $g \cdot cm^{-3}$	v_m $km \cdot sec^{-1}$	Θ_D^e K	Θ_D^c K	Source
Pyrope $Mg_3Al_2Si_3O_{12}$	3.563	5.589	789		Leitner, Weidner and Libermann (1980)
Cobalt olivine CO_2SiO_4	4.702	4.039	548		Sumino (1979)
Fayalite Fe_2SiO_4	4.397	3.786	507		Sumino (1979)
Forsterite Mg_2SiO_4	3.214	5.553	758,756	774	Graham and Barsch (1969), Sumino et al. (1977) Robie et al. (1982)
Tephroite Mn_2SiO_4	4.128	4.050	533		Sumino (1979)
Liebenbergite Ni_2SiO_4	4.933	4.464	615		Bass et al. (1984)
Spinel Ni_2SiO_4	5.351	4.997	708		Bass et al. (1984)
Zircon $ZrSiO_4$	4.649	5.351	718		Ozkan, Cartz and Jamieson (1974)
Wollastonite $CaSiO_3$	2.909			528	Krupka et al. (1985)
Ca-Al pyroxene $CaAl_2SiO_6$	3.435			820	Haselton, Hemingway and Robie (1983)
Hedenbergite $CaFeSi_2O_6$	3.657	4.564	619		Kandelin and Weidner (1988)

Table 1 (page 3)

Name and formula	Density $g \cdot cm^{-3}$	v_m $km \cdot sec^{-1}$	Θ_D^e K	Θ_D^c K	Source
Diopside $CaMgSi_2O_6$	3.277	4.989	668		Levien, Weidner and Prewitt (1979)
				580-650	Leadbetter et al. (1977)
Enstatite $MgSiO_3$	3.194	5.376	732		Weidner, Wang and Ito (1978)
Bronzite $Mg_{.96}Fe_{.06}SiO_3$	3.272	5.25	717		Duffy and Vaughan (1988)
Bronzite $Mg_{.8}Fe_{.2}SiO_3$	3.354	5.209	708		Frisillo and Barsch (1972)
Orthoferrosilite $FeSiO_3$	4.002	4.026	540		Bass and Weidner (1984)
Jadeite $NaAlSi_2O_6$	3.33	5.578	768		Kandelin and Weidner (1988)
Muscovite $KAl_2[AlSi_3O_{10}](OH)_2$	2.844	3.591	480		Vaughan and Guggenheim (1986)
Danburite $CaB_2Si_2O_8$	3.004	5.307	723		Ozkan and Cartz (1986)
Nepheline $KNa_3Al_4Si_4O_{16}$	2.571	3.961	500		Bonczar and Barsch (1975)

REFERENCES

Anderson, O.L., 1965, An approximate method of estimating shear velocity from specific heat. Journal of Geophysical Research, v. 70, p. 4726-4728.

Bass, J.D., 1986, Elasticity of uvarovite and andradite garnets. Journal of Geophysical Research, v. 91, p. 7505-7516.

Bass, J.D. and Weidner, D.J., 1984, Elasticity of single-crystal orthoferrosilite. Journal of Geophysical Research, v. 89, p. 4359-4371.

Bass, J.D., Weidner, D.J., Hamaya, N., Ozima, M. and Akimoto, S., 1984, Elasticity of the olivine and spinel polymorphs of Ni_2SiO_4. Physics and Chemistry of Minerals, v. 10, p. 261-272.

Bonczar, L.J. and Barsch, G.R., 1975, Elastic and thermoelastic constants of nepheline. Journal of Applied Physics, v. 46, p. 4339-4340.

Debye, P., 1912, Zur theorie der spezifischen Warmen. Annalen der Physik, v. 39, p. 789-839.

Duffy, T.S. and Vaughan, M.T., 1988, Elasticity of enstatite and its relationship to crystal structure. Journal of Geophysical Research, v. 93, p. 383-391.

Frisillo, A.L. and Barsch, G.R., 1972, Measurement of single-crystal elastic constants of bronzite as a function of temperature and pressure. Journal of Geophysical Research, v. 77, p. 6360-6384.

Graham, E.K. and Barsch, G.R., 1969, Elastic constants of single-crystal forsterite as a function of temperature and pressure. Journal of Geophysical Research, v. 74, p. 5949-5960.

Halleck, P.M., 1973, The compression and compressibility of grossularite garnet: a comparison of x-ray and ultrasonic methods. Ph.D. Thesis, University of Chicago, Chicago, Illinois.

Haselton, H.T., Jr., Hemingway, B.S. and Robie, R.A., 1983, Low-temperature heat capacities of $CaAl_2SiO_6$ glass and pyroxene and thermal expansion of $CaAl_2SiO_6$ pyroxene. American Mineralogist, v. 69, p. 481-489.

Hemingway, B.S., Barton, M.D., Robie, R.A. and Haselton, H.T., Jr., 1986, The heat capacity and thermodynamic functions for beryl, $Be_3Al_2Si_6O_{18}$, phenakite, Be_2SiO_4, euclase, $BeAlSi_4(OH)$, bertrandite, $Be_4Si_2O_7(OH)_4$, and chrysoberyl. American Mineralogist, v. 71, p. 557-568.

Kandelin, J. and Weidner, D.J., 1988, The single-crystal elastic properties of jadeite. Physics of the Earth and Planetary Interiors, v. 50, p. 251-260.

Kandelin, J. and Weidner, D.J., 1988, Elastic properties of hedenbergite. Journal of Geophysical Research, v. 93, p. 1063-1072.

Krupka, K.M., Robie, R.A., Hemingway, B.S., Kerrick, D.M. and Ito, J., 1985, Low-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, enstatite, and wollastonite. American Mineralogist, v. 70, p. 249-260.

Leadbetter, A.J., Jeapes, A.P., Waterfield, C.G. and Wycherley, K.E., 1977, The low temperature heat capacity of some glass ceramics. Chemical Physics Letters, v. 52, p. 469-471.

Leitner, B.J., Weidner, D.J. and Liebermann, R.C., 1980, Elasticity of single crystal pyrope and implications for garnet solid solution series. Physics of the Earth and Planetary Interiors, v. 22, p. 111-121.

Levien, L., Weidner, D.J. and Prewitt, C.T., 1979, Elasticity of diopside. Physics and Chemistry of Minerals, v. 4, p. 105-113.

Ozkan, H., Cartz, L., and Jamieson, J.C., 1974, Elastic constants of nonmetamict zirconium silicate. Journal of Applied Physics, v. 45, p. 556-562.

Ozkan, H. and Cartz, L., 1986, Elastic constants of calcium borosilicate ($CaB_2Si_2O_8$). High Temperatures - High Pressures, v. 18, p. 675-678.

Robie, R.A. and Edwards, J.L., 1966, Some Debye temperatures from single-crystal elastic constant data. Journal of Applied Physics, v. 37, p. 2659-2663.

Robie, R.A., Hemingway, B.S. and Takei, H., 1982, Heat capacities and entropies of Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_4 between 5 and 380 K. American Mineralogist, v. 67, p. 470-482.

Robie, R.A. and Hemingway, B.S., 1984, Entropies of kyanite, andalusite, and sillimanite: additional constraints on the pressure and temperature of the Al_2SiO_5 triple point. American Mineralogist, v. 69, p. 298-306.

Slater, J.C., 1939, Introduction to Chemical Physics. New York, McGraw-Hill, 521 p.

Sumino, Y., 1979, The elastic constants of Mn_2SiO_4, Fe_2SiO_4 and Co_2SiO_4 and the elastic properties of olivine group minerals at high temperature. Journal of the Physics of the Earth, v. 27, p. 209-238.

Sumino, Y., Nishizawa, O., Goto, T., Ohono, I. and Ozima, M., 1977, Temperature variation of elastic constants of single crystal forsterite between -190° and 400°C. Journal of the Physics of the Earth, v. 25, p. 377-392.

Tatli, A., 1985, Zero-field elastic constants of uvite. Journal of Physics and Chemistry of Solids, v. 46, p. 1015-1018.

Vaughan, M.T. and Weidner, D.J., 1978, The relationship of elasticity and crystal structure in andalusite and sillimanite. Physics and Chemistry of Minerals, v. 3, p. 133-144.

Vaughan, M.T. and Guggenheim, S., 1986, Elasticity of muscovite and its relationship to crystal structure. Journal of Geophysical Research, v. 91, p. 4657-4664.

Weidner, D.J. and Carleton, H.R., 1977, Elasticity of coesite. Journal of Geophysical Research, v. 82, p. 1334-1346.

Weidner, D.J., Swyler, K. and Carleton, H.R., 1975, Elasticity of microcrystals. Geophysical Research Letters, v. 2, p. 189-192.

Weidner, D.J., Wang, H. and Ito, J., 1978, Elasticity of orthoenstatite. Physics of the Earth and Planetary Interiors, v. 17, p. 7-13.

Weidner, D.J., Bass, J.D., Rigwood, A.E. and Sinclair, W., 1982, The single-crystal elastic module of stishovite. Journal of Geophysical Research, v. 87, p. 4740-4746.

Yeganek-Haeri, A. and Weidner, D.J., 1985, Single crystal elastic moduli of a beryllium silicate: phenacite (Be_2SiO_4). EOS, v. 66, p. 358.

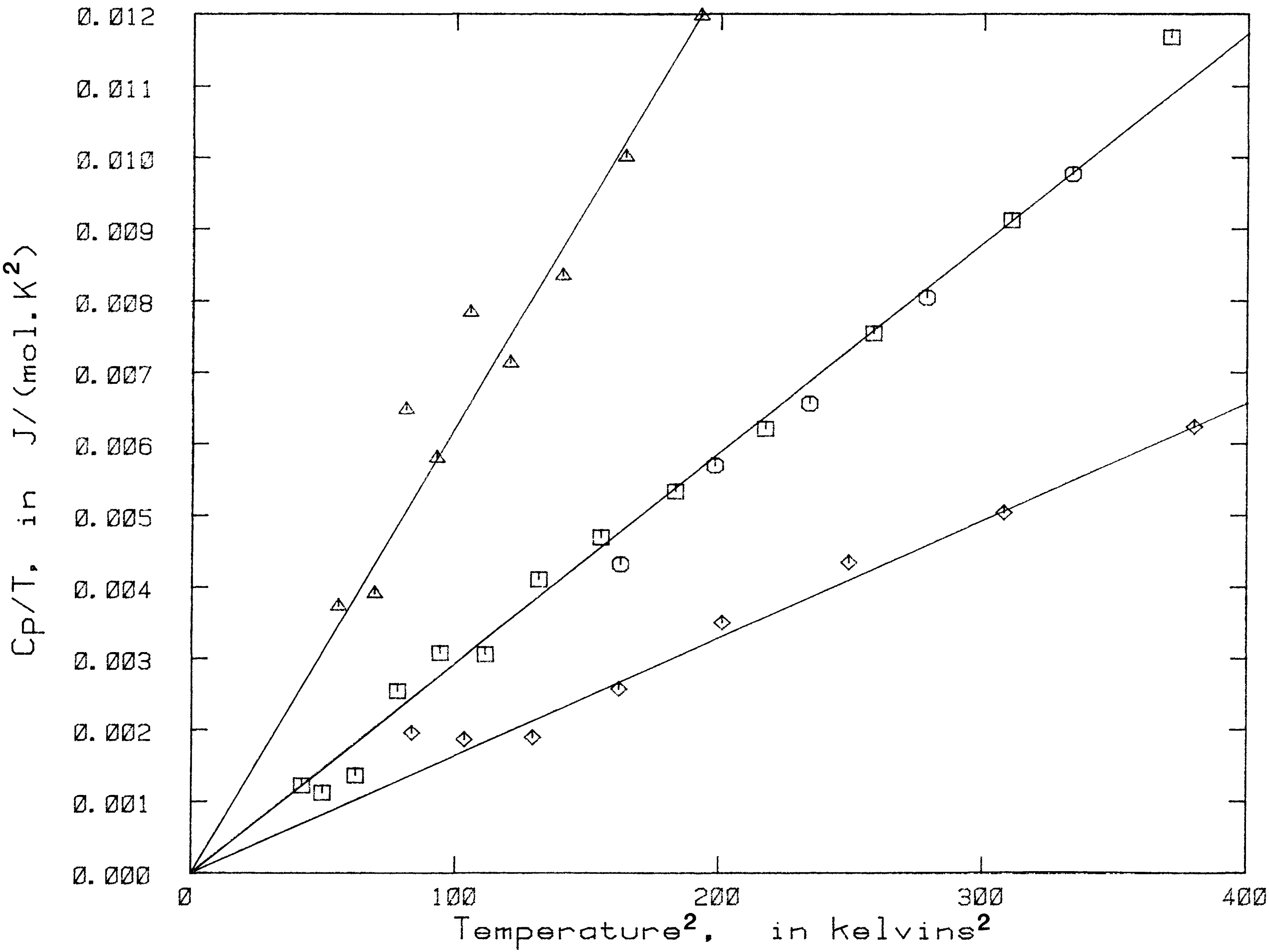
Yoon, H.S. and Newnham, R.E., 1973, The elastic properties of beryl. Acta Crystallographica, v. A29, p. 507-509.

Zemansky, M.W., 1968, Heat and Thermodynamics (Fifth Edition). New York, McGraw-Hill, 657 p.

FIGURE CAPTIONS

Figure 1. Low-temperature molar heat capacities for enstatite (squares) and wollastonite (triangles) from Krupka et al. (1985) and for phenakite (diamonds) from Hemingway et al. (1986) plotted as C_p°/T against T^2 for $T < \Theta_D/35$. Solid straight line correspond to calculated values using Θ_D = 939 K for phenakite, 692 K for enstatite, and 539 K for wollastonite.

Figure 2. Velocity of sound in muscovite in km/sec in the (010) plane calculated from the elastic constants of Vaughan and Guggenheim (1986).



0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
Cp/T, in J/(mol.K²)
0
100
200
300
400
Temperature², in kelvins²

Figure 1

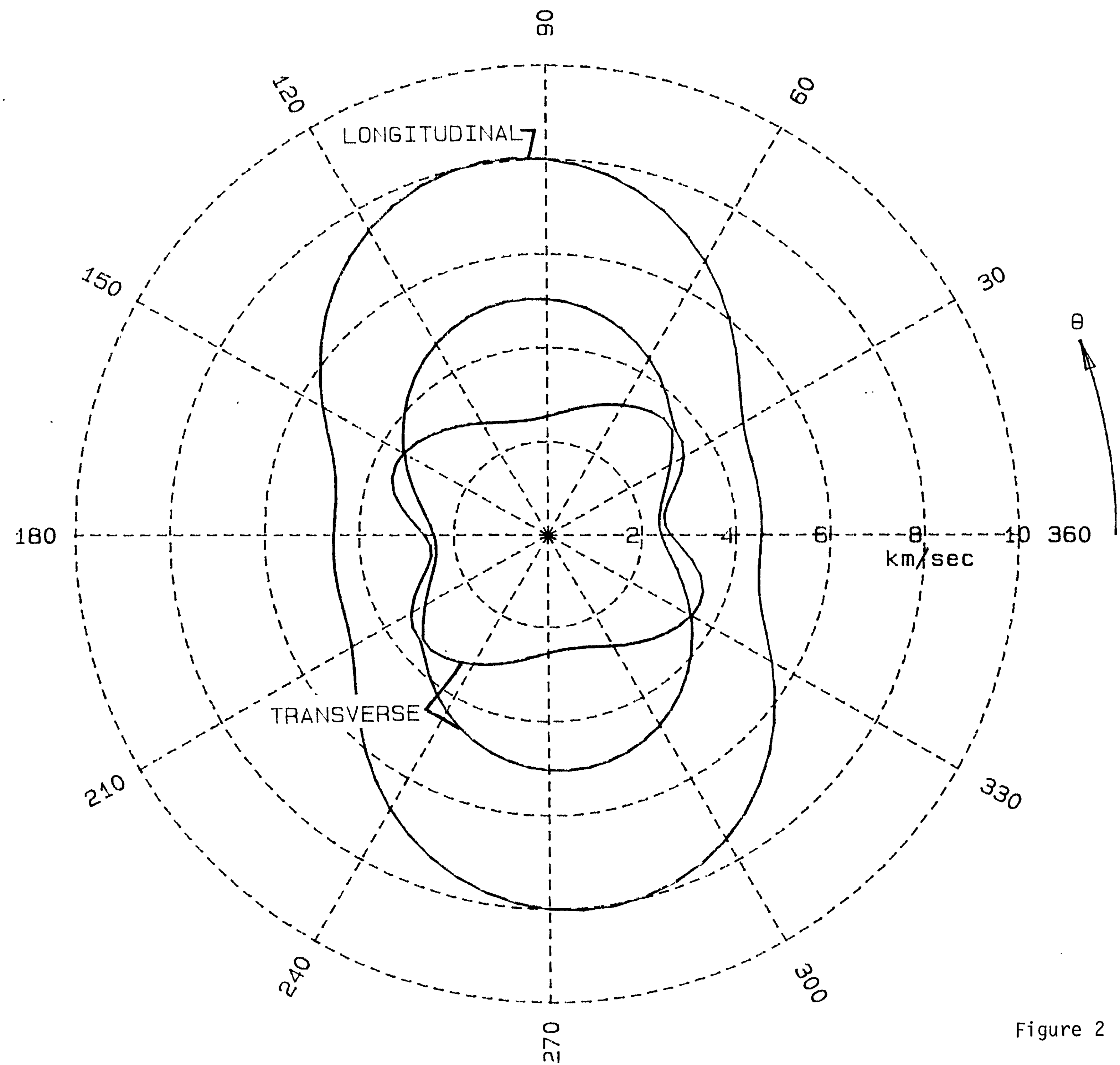

90
60
30
360
330
300
270
240
210
180
150
120
θ
2
4
6
8
10
km/sec
LONGITUDINAL
TRANSVERSE

Figure 2

APPENDIX

A computer program was written in BASIC to calculate the mean velocity of sound given values for the single crystal elastic constants using the relations given by Robie and Edwards (1966). The program was written for a Hewlett-Packard 9826 computer. A listing of the computer program is given as Table 2.

In response to the request by the computer, the user supplies the name, crystal density, crystal system, number of atoms in the formula, indicates whether the elastic constants are the stiffnesses (c_{ij}) or compliances (s_{ij}) and the initial, final and incremental values for the azimuthal angle Φ, and similarly for the zenith angle Θ. The computer then solves for the 3 roots of equation (6) at each of the specified values of Θ and Φ and numerically evaluates the following expression

$$3/v_m{}^3 = \int_0^{4\pi}[(1/v_1^3) + (1/v_2^3) + (1/v_3^3)](d\Omega/4\pi), \qquad (7)$$

where v_1, v_2, and v_3 are the roots of Eq. (5) and $d\Omega$ is the differential solid angle

$$d\Omega = \sin\Theta d\Theta d\Phi. \qquad (8)$$

to obtain the mean velocity of sound, and hence the Debye temperature.

The program lists the values for the sound velocity (two shear wave velocities and one longitudinal velocity) at each specified Θ and Φ. It can also generate a file of these velocities on a floppy fisk for use with a subsidiary plotting program.

```
10    REM CRYSTAL WAVE VELOCITIES AND DEBYE TEMPS REVISED 12/2/1988
20    DIM C(6,6),S(6,6),G(3,3),V(3),A1(73,73),A2(73,73),A3(73,73),A4(73,73),P1$[
14],Name$[60]
30    PRINT "NAME AND OTHER INFORMATION?"
40    INPUT Name$
50    PRINT "DATE  MM/DD/YY"
60    INPUT Day$
70    PRINT "CRYSTAL SYSTEM CAN ONLY HAVE THE NAMES: CUBIC, TET, HEX, ORTH, MON,
TRIG"
80    PRINT "CRYSTAL SYSTEM?"
90    INPUT System$
100   P1$="2(3D),3(2D.3D)"
110   Avog=6.022094E+23
120   Hk=4.799281E-11
130   REM PRINT "IF THE ELASTIC CONSTANTS ARE S(I,J) AND NOT C(I,J) ENTER 1"
140   REM INPUT Jjjj
150   PRINT "DENSITY?"
160   INPUT Rho
170   PRINT "NUMBER OF ATOMS IN FORMULA?"
180   INPUT Iq
190   PRINT "ENTER 1 TO GENERATE A PLOTTING FILE OR ENTER 0 TO CALCULATE DEBYE T
"
200   INPUT Yyyy
210   PRINT "IF YOU WISH TO PLOT INSERT A FORMATTED DISK AND PRESS CONTINUE"
220   PAUSE
230   IF Yyyy=0 THEN 310
240   Tmin=0
250   Tm=360
260   Dt=5
270   Pmin=0
280   Pm=360
290   Dp=5
300   GOTO 450
310   PRINT "FORMULA WEIGHT, IN GRAMS"
320   INPUT Formwt
330   PRINT "THETA MINIMUM ?"
340   INPUT Tmin
350   PRINT "THETA MAXIMUM ?"
360   INPUT Tm
370   PRINT "THETA INCREMENT ?"
380   INPUT Dt
390   PRINT "PHI MINIMUM ?"
400   INPUT Pmin
410   PRINT "PHI MAXIMUM ?"
420   INPUT Pm
430   PRINT "PHI INCREMENT ?"
440   INPUT Dp
450   Sy=360./Pm*180./Tm
460   St=0
470   Sl=0
480   Sm=0
490   P=.01745329
500   Dtt=Dt
510   Dt=Dt*P
520   Dpp=Dp
530   Dp=Dp*P
540   IF System$="CUBIC" THEN 560
550   IF System$<>"CUBIC" THEN 690
560   PRINT "C(1,1) ?"
570   INPUT C(1,1)
580   PRINT "C(1,2) ?"
590   INPUT C(1,2)
```

```
600   PRINT "C(4,4) ?"
610   INPUT C(4,4)
620   C(2,2)=C(1,1)
630   C(3,3)=C(2,2)
640   C(5,5)=C(4,4)
650   C(6,6)=C(5,5)
660   C(1,3)=C(1,2)
670   C(2,3)=C(1,3)
680   GOTO 1830
690   IF System$="ORTH" THEN 710
700   IF System$<>"ORTH" THEN 900
710   PRINT "C(1,1) ?"
720   INPUT C(1,1)
730   PRINT "C(2,2) ?"
740   INPUT C(2,2)
750   PRINT "C(3,3) ?"
760   INPUT C(3,3)
770   PRINT "C(4,4) ?"
780   INPUT C(4,4)
790   PRINT "C(5,5) ?"
800   INPUT C(5,5)
810   PRINT "C(6,6) ?"
820   INPUT C(6,6)
830   PRINT "C(1,2) ?"
840   INPUT C(1,2)
850   PRINT "C(1,3) ?"
860   INPUT C(1,3)
870   PRINT "C(2,3) ?"
880   INPUT C(2,3)
890   GOTO 1830
900   IF System$="TET" THEN 920
910   IF System$<>"TET" THEN 1110
920   PRINT "C(1,1) ?"
930   INPUT C(1,1)
940   PRINT "C(3,3) ?"
950   INPUT C(3,3)
960   PRINT "C(4,4) ?"
970   INPUT C(4,4)
980   PRINT "C(6,6) ?"
990   INPUT C(6,6)
1000  PRINT "C(1,2) ?"
1010  INPUT C(1,2)
1020  PRINT "C(1,3) ?"
1030  INPUT C(1,3)
1040  PRINT "C(1,6) ?"
1050  INPUT C(1,6)
1060  C(2,2)=C(1,1)
1070  C(2,3)=C(1,3)
1080  C(5,5)=C(4,4)
1090  C(2,6)=-C(1,6)
1100  GOTO 1830
1110  IF System$="HEX" THEN 1130
1120  IF System$<>"HEX" THEN 1280
1130  PRINT "C(1,1)"
1140  INPUT C(1,1)
1150  PRINT "C(3,3) ?"
1160  INPUT C(3,3)
1170  PRINT "C(4,4) ?"
1180  INPUT C(4,4)
```

```
1190  PRINT "C(1,2) ?"
1200  INPUT C(1,2)
1210  PRINT "C(1,3) ?"
1220  INPUT C(1,3)
1230  C(2,2)=C(1,1)
1240  C(2,3)=C(1,3)
1250  C(5,5)=C(4,4)
1260  C(6,6)=1/2*(C(1,1)-C(1,2))
1270  GOTO 1830
1280  IF System$="TRIG" THEN 1300
1290  IF System$<>"TRIG" THEN 1530
1300  PRINT "C(1,1) ?"
1310  INPUT C(1,1)
1320  PRINT "C(3,3) ?"
1330  INPUT C(3,3)
1340  PRINT "C(4,4) ?"
1350  INPUT C(4,4)
1360  PRINT "C(1,2) ?"
1370  INPUT C(1,2)
1380  PRINT "C(1,3) ?"
1390  INPUT C(1,3)
1400  PRINT "C(1,4) ?"
1410  INPUT C(1,4)
1420  PRINT "C(2,5) ?"
1430  INPUT C(2,5)
1440  C(2,2)=C(1,1)
1450  C(5,5)=C(4,4)
1460  C(2,3)=C(1,3)
1470  C(2,4)=-C(1,4)
1480  C(1,5)=-C(2,5)
1490  C(6,6)=1/2*(C(1,1)-C(1,2))
1500  C(4,6)=C(2,5)
1510  C(5,6)=-C(2,4)
1520  GOTO 1830
1530  IF System$="MON" THEN 1550
1540  IF System$<>"MON" THEN 1820
1550  PRINT "C(1,1) ?"
1560  INPUT C(1,1)
1570  PRINT "C(2,2) ?"
1580  INPUT C(2,2)
1590  PRINT "C(3,3) ?"
1600  INPUT C(3,3)
1610  PRINT "C(4,4) ?"
1620  INPUT C(4,4)
1630  PRINT "C(5,5) ?"
1640  INPUT C(5,5)
1650  PRINT "C(6,6) ?"
1660  INPUT C(6,6)
1670  PRINT "C(1,2) ?"
1680  INPUT C(1,2)
1690  PRINT "C(1,3) ?"
1700  INPUT C(1,3)
1710  PRINT "C(2,3) ?"
1720  INPUT C(2,3)
1730  PRINT "C(1,5) ?"
1740  INPUT C(1,5)
1750  PRINT "C(2,5) ?"
1760  INPUT C(2,5)
1770  PRINT "C(3,5) ?"
```

```
1780  INPUT C(3,5)
1790  PRINT "C(4,6) ?"
1800  INPUT C(4,6)
1810  GOTO 1830
1820  PRINT "INCORRECT LABEL FOR CRYSTAL SYSTEM"
1830  FOR I=1 TO 5
1840  FOR J=1 TO I
1850  C(I+1,J)=C(J,I+1)
1860  NEXT J
1870  NEXT I
1880  MAT S= INV(C)
1890  Compress=S(1,1)+S(2,2)+S(3,3)+2*(S(1,2)+S(2,3)+S(3,1))
1900  REM IF Jjjj=0 THEN 1820
1910  REM FOR I=1 TO 6
1920  REM FOR J=1 TO 6
1930  REM S(I,J)=C(I,J)
1940  REM NEXT J
1950  REM NEXT I
1960  REM MAT C= INV(S)
1970  PRINTER IS 10;WIDTH 80
1980  REM ***CALCULATE GAMMA(I,J) VALUES***
1990  M=0
2000  N=0
2010  FOR I=Tmin TO Tm STEP Dtt
2020  Theta=I*P
2030  M=M+1
2040  FOR J=Pmin TO Pm STEP Dpp
2050  Phi=J*P
2060  N=N+1
2070  REM SUBROUTINE GAMMA
2080  E11=SIN(Theta)*COS(Phi)
2090  E12=SIN(Theta)*SIN(Phi)
2100  E13=COS(Theta)
2110  E111=E11^2
2120  E122=E12^2
2130  E133=E13^2
2140  E112=E11*E12
2150  E123=E12*E13
2160  E131=E13*E11
2170  G(1,1)=E111*C(1,1)+E122*C(6,6)+E133*C(5,5)+E123*2.*C(5,6)+E131*2.*C(1,5)+E
112*2.*C(1,6)
2180  G(2,2)=E111*C(6,6)+E122*C(2,2)+E133*C(4,4)+E123*2.*C(2,4)+E131*2.*C(4,6)+E
112*2.*C(2,6)
2190  G(3,3)=E111*C(5,5)+E122*C(4,4)+E133*C(3,3)+E123*2.*C(3,4)+E131*2.*C(3,5)+E
112*2.*C(4,5)
2200  G(1,2)=E111*C(1,6)+E122*C(2,6)+E133*C(4,5)
2210  G(1,2)=G(1,2)+E123*(C(4,6)+C(2,5))+E131*(C(5,6)+C(1,4))+E112*(C(1,2)+C(6,6
))
2220  G(2,3)=E111*C(5,6)+E122*C(2,4)+E133*C(3,4)
2230  G(2,3)=G(2,3)+E123*(C(2,3)+C(4,4))+E131*(C(4,5)+C(3,6))+E112*(C(4,6)+C(2,5
))
2240  G(3,1)=E111*C(1,5)+E122*C(4,6)+E133*C(3,5)+E123*(C(4,5)+C(3,6))+E131*(C(1,
3)+C(5,5))
2250  G(3,1)=G(3,1)+E112*(C(5,6)+C(1,4))
2260  G(2,1)=G(1,2)
2270  G(3,2)=G(2,3)
2280  G(1,3)=G(3,1)
2290  REM ***EVALUATE ROOTS OF CUBIC EQUATION***
2300  Alph=-1.
2310  Beta=G(1,1)+G(2,2)+G(3,3)
2320  Gamm=G(1,2)^2+G(2,3)^2+G(3,1)^2-G(2,2)*G(3,3)-G(1,1)*G(3,3)-G(1,1)*G(2,2)
```

```
2330  Delta=G(1,1)*G(2,2)*G(3,3)+2.*G(1,2)*G(2,3)*G(3,1)-G(1,2)^2*G(3,3)-G(2,3)^
2*G(1,1)
2340  Delta=Delta-(G(3,1)^2)*G(2,2)
2350  H=(3.*Alph*Gamm-Beta^2)/9./Alph^2
2360  W=(Beta/100.)^3
2370  W=2.*W/27./Alph^3
2380  W=W*(100.)^3
2390  G1=W+(-Alph*Beta*Gamm/3.+Alph^2*Delta)/Alph^3
2400  Alp=-G1/2./SQR(ABS(H))^3
2410  Aalp=ABS(Alp)
2420  IF (Aalp-1.)<0 THEN GOTO 2480
2430  IF (Aalp-1.)>=0 THEN GOTO 2440
2440  Alfa=0
2450  IF (Alp)<0 THEN GOTO 2470
2460  IF (Alp)>=0 THEN GOTO 2490
2470  Alfa=(180.*1.745329E-2)
2480  Alfa=(90.*1.745329E-2)-ATN(Alp/(1.-Alp^2)^.5)
2490  Alfha=Alfa/3.
2500  Am=2.*SQR(-H)
2510  Z1=Am*COS(Alfha)
2520  Z2=Am*COS(Alfha+2.094395)
2530  Z3=Am*COS(Alfha+4.188790)
2540  X1=Z1-Beta/3./Alph
2550  X2=Z2-Beta/3./Alph
2560  X3=Z3-Beta/3./Alph
2570  X1=(SQR(X1/Rho))*1.E+1
2580  X2=(SQR(X2/Rho))*1.E+1
2590  X3=(SQR(X3/Rho))*1.E+1
2600  REM ***SORT VELOCITIES AS V(3)>V(2)>V(1)***
2610  V1=X1
2620  V2=X2
2630  V3=X3
2640  IF V1<=V2 THEN GOTO 2670
2650  V1=X2
2660  V2=X1
2670  IF V2<=V3 THEN GOTO 2710
2680  X1=V2
2690  V2=V3
2700  V3=X1
2710  IF V1<=V2 THEN GOTO 2750
2720  X1=V2
2730  V2=X1
2740  V1=X1
2750  Rav=1/V1^3+1/V2^3+1/V3^3
2760  A1(M,N)=V1
2770  A2(M,N)=V2
2780  A3(M,N)=V3
2790  A4(M,N)=Rav
2800  REM ***NUMERICAL INTEGRATION FOR V(MEAN)***
2810  Th=Theta
2820  Dw=(COS(Th)-COS(Th+Dt))*Dp
2830  IF J=Pm THEN 2880
2840  IF I=Tm THEN 2880
2850  St=St+(1./V1^3+1./V2^3)*Dw
2860  Sl=Sl+Dw/V3^3
2870  Sm=Sm+Rav*Dw
2880  NEXT J
2890  N=0
2900  NEXT I
```

```
2910  IF Yyyy=0 THEN 3220
2920  REM  ** GENERATE PLOTTING FILES **
2930  ASSIGN @F1 TO "VEL1_DAT"
2940  R=19
2950  L=73
2960  Kk=0
2970  FOR N=1 TO L
2980  Ph=(N-1)*Dpp
2990  Kk=Kk+1
3000  OUTPUT @F1,Kk USING P1$;90,Ph,A1(R,N),A2(R,N),A3(R,N),A4(R,N)
3010  NEXT N
3020  ASSIGN @F1 TO *
3030  ASSIGN @F1 TO "VEL2_DAT"
3040  Kk=0
3050  I=1
3060  FOR N=1 TO 73
3070  Tht=(N-1)*Dtt
3080  Kk=Kk+1
3090  OUTPUT @F1,Kk USING P1$;Tht,0,A1(N,I),A2(N,I),A3(N,I),A4(N,I)
3100  NEXT N
3110  ASSIGN @F1 TO *
3120  ASSIGN @F1 TO "VEL3_DAT"
3130  Kk=0
3140  N=19
3150  FOR K=1 TO 73
3160  Tht=(K-1)*Dtt
3170  Kk=Kk+1
3180  OUTPUT @F1,Kk USING P1$;Tht,90,A1(K,N),A2(K,N),A3(K,N),A4(K,N)
3190  NEXT K
3200  ASSIGN @F1 TO *
3210  GOTO 4210
3220  Vt=((Sy/12.56637*St)/2.)^(-.3333333)
3230  Vl=(Sy/12.56637*Sl)^(-.3333333)
3240  Vm=((Sy/12.56637*Sm)/3.)^(-.3333333)
3250  Debye=Hk*(3.*Iq*Avog*Rho/12.56637/Formwt)^.3333333*Vm*100000
3260  REM ***PRINTOUT OF C(I,J)'S AND VELOCITIES***
3270  PRINT Name$,Day$
3280  PRINT
3290  PRINT USING "10A,2X,DD.DDDD,2X,7A";"DENSITY---",Rho,"GM/CM^3"
3300  PRINT
3310  PRINT USING "16A,2X,DDD.DDD,2X,7A";"FORMULA WEIGHT--",Formwt,"GM/MOLE"
3320  PRINT
3330  PRINT USING "30A,2X,DDD";"NUMBER OF ATOMS IN MOLECULE--",Iq
3340  PRINT
3350  PRINT "INTEGRATION IN THETA AND PHI"
3360  PRINT
3370  PRINT USING "34A,X,DD.DDDD,X,6A";"MEAN VELOCITY OF TRANSVERSE WAVES--",Vt,
"KM/SEC"
3380  PRINT
3390  PRINT USING "35A,X,DD.DDDD,X,6A";"MEAN VELOCITY OF LONGITUDINAL WAVE--",Vl
,"KM/SEC"
3400  PRINT
3410  PRINT USING "19A,X,DD.DDDD,X,6A";"MEAN SOUND VELOCITY--",Vm,"KM/SEC"
3420  PRINT
3430  PRINT USING "19A,X,DDDD.D,X,6A";"DEBYE TEMPERATURE--",Debye,"KELVIN"
3440  PRINT
3450  PRINT USING "17A,X,DD.DD,X,6A";"COMPRESSIBILITY--",Compress,"1/MBAR"
3460  PRINT
3470  PRINT "THE C(I,J) IN MEGABARS"
```

```
3480  PRINT
3490  PRINT USING "XX,DD.DDDD";C(1,1),C(1,2),C(1,3),C(1,4),C(1,5),C(1,6)
3500  PRINT USING "11X,4(DD.4D,XX),DD.4D";C(2,2),C(2,3),C(2,4),C(2,5),C(2,6)
3510  PRINT USING "20X,3(DD.4D,XX),DD.DDDD";C(3,3),C(3,4),C(3,5),C(3,6)
3520  PRINT USING "29X,DD.DDDD,XX,DD.DDDD,XX,DD.DDDD";C(4,4),C(4,5),C(4,6)
3530  PRINT USING "38X,DD.DDDD,XX,DD.DDDD";C(5,5),C(5,6)
3540  PRINT USING "47X,DD.DDDD";C(6,6)
3550  PRINT
3560  PRINT
3570  PRINT "THE S(I,J) IN RECIPROCAL MEGABARS"
3580  PRINT
3590  PRINT USING "XX,DD.DDDD";S(1,1),S(1,2),S(1,3),S(1,4),S(1,5),S(1,6)
3600  PRINT USING "11X,4(DD.4D,XX),DD.4D";S(2,2),S(2,3),S(2,4),S(2,5),C(2,6)
3610  PRINT USING "20X,3(DD.4D,XX),DD.DDDD";S(3,3),S(3,4),S(3,5),S(3,6)
3620  PRINT USING "29X,DD.DDDD,XX,DD.DDDD,XX,DD.DDDD";S(4,4),S(4,5),S(4,6)
3630  PRINT USING "38X,DD.DDDD,XX,DD.DDDD";S(5,5),S(5,6)
3640  PRINT USING "47X,DD.DDDD";S(6,6)
3650  PRINT
3660  PRINT
3670  PRINT
3680  PRINT "SOUND WAVE VELOCITY (IN KM/SEC) AS A FUNCTION OF THETA AND PHI IN T
HE XY PLANE"
3690  PRINT
3700  PRINT "                    **TRANSVERSE**   LONGITUDINAL   RECIPROCIAL AVERAG
E"
3710  PRINT "THETA     PHI       V1        V2           V3     (1/V1^3+1/V2^3+1/V3^
3)"
3720  PRINT
3730  PRINT
3740  IF Tm<>180 THEN 3780
3750  IF Dtt=5 THEN K=19
3760  IF Dtt=10 THEN K=10
3770  GOTO 3790
3780  K=Tm/Dtt+1
3790  R=K
3800  L=Pm/Dpp+1
3810  FOR N=1 TO L
3820  Ph=(N-1)*Dpp
3830  IMAGE DDD.D,XXX,DDD.D,XXX,DD.DDD,XXX,DD.DDD.XXXXXX,DD.DDD,9X,.DDDDDE
3840  PRINT USING 3830;90,Ph,A1(R,N),A2(R,N),A3(R,N),A4(R,N)
3850  NEXT N
3860  PRINT
3870  PRINT
3880  PRINT
3890  PRINT
3900  PRINT "SOUND WAVE VELOCITY (IN KM/SEC) AS A FUNCTION OF THETA AND PHI IN T
HE XZ PLANE"
3910  PRINT
3920  PRINT "                    **TRANSVERSE**   LONGITUDINAL   RECIPROCIAL AVERAG
E"
3930  PRINT "THETA     PHI       V1        V2           V3     (1/V1^3+1/V2^3+1/V3^
3)"
3940  PRINT
3950  PRINT
3960  I=1
3970  K=Tm/Dtt+1
3980  FOR N=1 TO K
3990  Tht=(N-1)*Dtt
4000  PRINT USING 3830;Tht,Pmin,A1(N,I),A2(N,I),A3(N,I),A4(N,I)
4010  NEXT N
4020  PRINT
4030  PRINT
```

```
4040  PRINT "SOUND WAVE VELOCITY (IN KM/SEC) AS A FUNCTION OF THETA AND PHI IN T
HE YZ PLANE"
4050  PRINT "THETA     PHI       V1        V2            V3     (1/V1^3+1/V2^3+1/V3^
3)"
4060  PRINT
4070  PRINT
4080  IF Pm<>180 THEN 4120
4090  IF Dpp=5 THEN L=19
4100  IF Dpp=10 THEN L=10
4110  GOTO 4160
4120  IF Pm<>120 THEN 4160
4130  IF Dpp=5 THEN L=19
4140  IF Dpp=10 THEN L=10
4150  GOTO 4160
4160  N=L
4170  FOR K=1 TO K
4180  Tht=(K-1)*Dtt
4190  PRINT USING 3830;Tht,90,A1(K,N).A2(K,N),A3(K,N),A4(K,N)
4200  NEXT K
4210  PRINTER IS 1;WIDTH 50
4220  END
```