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THE LATTICE PARAMETERS AND STRUCTURES OF IRON-SILICON
SINGLE CRYSTALS AND THE ELASTIC CONSTANTS OF Fe_3Si

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The lattice parameters and structures of iron-silicon
single crystals and the elastic constants of Fe_3Si

by

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THE LATTICE PARAMETERS AND STRUCTURES OF IRON-SILICON
SINGLE CRYSTALS AND THE ELASTIC CONSTANTS OF Fe_3Si^*

John Bernard Rausch

The room temperature lattice parameters of thirteen slowly cooled iron-silicon single crystals containing from 3.61 to 25 atom percent silicon were measured. In addition, x-ray diffraction patterns were obtained from (100), (110) and (111) faces of each crystal. The lattice parameter versus composition curve has a newly discovered, and well defined, plateau extending from approximately 9.5 to 12 atom percent silicon. The inflection point at 9.5 atom percent silicon coincides with the first observance of superlattice reflections in these alloys. The inflection point at 12 atom percent silicon coincides with known changes in slope in the composition dependence of both the electrical resistivity and the elastic constants.

In addition the elastic constants of a Fe_3Si single crystal were measured over the temperature range of 4.2 to 300 degrees Kelvin. The electrical resistivity of this same alloy was also measured over the temperature range of 4.2 to 400 degrees Kelvin.

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INTRODUCTION

Iron-silicon alloys of approximately 1.5 to 7 atom percent silicon are of great commercial importance, primarily in the electrical machinery industry (1,2,3,4). This is best illustrated by the 1970 silicon-iron electrical steel production of 750,000 tons (3). A cast alloy based on the Fe_3Si composition is also extensively used for handling corrosive liquids (5,6).

Despite the obvious commercial importance of this system, the equilibrium solid state structural relationships remain unresolved. These relationships as represented in several recent reviews (7,8,9) are in obvious disagreement as is shown in Figure 1. In the composition range of zero to 25 atom percent silicon two phases are known to exist at room temperature. These are (i) α which is a body centered cubic substitutional solid solution of silicon in iron, (ii) α_1 which is a long range ordered structure of the DO_3 type. A third structure α_2 , which is also long range ordered with a B2 structure, is known to exist at high temperatures (10). Although it is not shown here, recent theoretical calculations of the expected structures and boundaries for this system lead to still another representation (11). One point that does appear to be clear from electrical resistivity, x-ray diffraction (12), and elastic constant measurements (F. X. Kayser, Iowa State University, unpublished data, 1975), is that alloys

Figure 1. Portions of the iron-silicon phase diagram:
(a) as presented by Hansen (7)
(b) as presented by Hultgren (8)

containing greater than approximately 11.8 atom percent silicon are long range ordered.

The primary purpose of this investigation was to use conventional x-ray techniques and single crystal specimens to ascertain the structures and the lattice parameters of very slowly cooled iron-silicon alloys. As an additional method in determining the boundaries between the different structures present, the electrical resistivity as a function of composition was measured on pieces cut from the single crystals used in the x-ray investigation. The composition of these alloys covers the range of 3.61 to 24.85 atom percent silicon.

The elastic constants are important thermodynamic parameters. These parameters are doubly important for Fe_3Si because of its commercial importance. As there were no published constants for this alloy, a complementary investigation aimed at determining these constants was undertaken. The elastic constants were measured as a function of temperature from 4.2 to 300 degrees Kelvin. In addition the electrical resistivity of a sample cut from the same crystal was determined over the temperature range of 4.2 to 400 degrees Kelvin.

SAMPLE PREPARATION AND ANALYSIS

All samples with the exception of numbers 11 and 12 in Table 1 were prepared at Ames Laboratory from electrolytic iron from The Glidden Company and semiconductor grade silicon from Texas Instruments Company. For each alloy two or three button shaped ingots of approximately 40 grams mass were prepared by arc-melting. These buttons were sectioned into small pieces and charged into a crucible for growth by the Bridgman method. The alloy was completely melted in the crucible and then drawn out of the hot zone of the furnace at a rate of one-quarter of an inch per hour. During this entire process a helium inert gas atmosphere was maintained in the furnace. The crucible materials used for the various alloys are given in Table 1. Crystals 11 and 12 were obtained from Dr. F. X. Kayser.

All the crystals were given a homogenization anneal of a minimum of 24 hours at 1000 degrees Celsius. The crystals were oriented by x-ray methods and sets of parallel faces were cut on an electromachining apparatus. All crystals were cut with a set of parallel faces perpendicular to the $[110]$ direction and most also have sets of faces perpendicular to both the $[\bar{1}10]$ and $[001]$ directions. The cut faces were polished through 600 grit paper and were electropolished to remove any trace of cold work. The dimensions and masses of these cut crystals are given in Table 1. The crystals were given an

Table 1. The mass and dimensions of the iron-silicon single crystals

Sample number	Mass (grams)	Dimensions (mm)			Crucible material ^a
		(110)	($\bar{1}10$)	(001)	
1	8.53	10.90	12.10	8.44	Z
2	14.61	15.64	10.54	11.62	Z
3	13.11	15.30	8.96	12.71	Z
4	12.95	9.93	12.93	13.59	Z
5	19.12	9.81	15.79	16.43	Z
6	27.80	14.04	-	12.30	M
7	13.16	12.37	11.15	-	Z
8	18.58	15.84	11.85	13.47	Z
9	40.34	15.46	21.46	18.17	Z
10	17.15	16.82	10.97	12.81	Z
11	14.11	7.00	-	-	Z
12	19.79	8.33	-	-	Z
13	12.10	8.54	14.28	14.59	Z

^aZ represents a 1 inch diameter, 3 inch long CaO-stabilized zirconia crucible with a conical tip. M represents a 3/4 inch diameter by 3 inch long, flat-bottomed, magnesia crucible.

ordering anneal consisting of heating to 580 degrees Celsius and cooling to room temperature at the rate of 10 degrees per day.

Chemical analysis was done by the analytical chemistry group of Ames Laboratory on pieces cut from the crystals. Several separate analyses were made on each sample. These results were averaged by using the mass of the piece analyzed as a weighting factor. The results of the analyses, the average value of composition and the standard deviation of the results are given in Table 2 for each sample.

Table 2. The chemical analyses of the iron-silicon single crystals

Sample	Mass analyzed (grams)	Weight percent silicon	Average weight percent	Average atom percent	St. dev. atom percent
1	2.0174	1.87	1.85	3.61	0.18
	1.7189	1.93			
	0.2089	1.84			
	0.2511	1.51			
	0.4702	1.80			
	0.4429	1.80			
	0.1064	1.65			
2	1.3520	2.80	2.83	5.47	0.17
	1.3588	2.90			
	0.3254	2.64			
	0.2509	2.78			
	0.2992	2.72			
	0.1693	3.00			
	0.1948	2.88			
3	0.9862	4.96	4.60	8.75	0.59
	1.0451	4.49			
	1.0260	4.61			
	0.9354	4.43			
	0.2356	4.50			
	0.2331	4.47			
	0.1504	4.49			
4	0.1958	4.59	4.99	9.46	0.16
	0.7199	4.86			
	0.7511	4.82			
	0.2153	4.76			
	0.2485	4.87			
	0.2664	4.93			
	0.2301	4.88			
5	3.8300	5.04	5.59	10.53	0.24
	3.3944	5.04			
	0.8472	5.65			
	0.8983	5.58			
	0.2081	5.41			
	0.2074	5.48			
	0.2380	5.50			
	0.0855	6.06	5.59	10.53	0.24
	0.0857	5.61			

Table 2. (Continued)

Sample	Mass analyzed (grams)	Weight percent silicon	Average weight percent	Average atom percent	St. dev. atom percent
6	4.7567	6.87	6.57	12.27	0.58
	4.0732	6.14			
	3.6429	6.67			
7	0.6110	8.74	8.50	15.59	0.46
	0.5462	8.72			
	0.5060	8.62			
	0.2112	8.08			
	0.2151	7.89			
	0.1368	8.38			
	0.1543	7.86			
8	0.5303	9.73	9.63	17.48	0.19
	0.5057	9.62			
	0.2071	9.53			
	0.2378	9.42			
	0.3533	9.74			
	0.3944	9.58			
9	2.8100	10.84	11.11	19.91	0.10
	3.7334	11.16			
	5.8274	11.16			
	5.5097	11.15			
10	0.4842	12.32	12.18	21.62	0.25
	0.4866	12.17			
	0.2433	12.22			
	0.2835	11.92			
11	0.5321	13.99	13.95	24.38	0.07
	0.5302	13.91			
12	0.5144	13.93	13.88	24.27	0.10
	0.5007	13.82			
13	0.4970	14.18	14.26	24.85	0.32
	0.5056	14.13			
	0.1623	14.27			
	0.1471	13.88			
	0.2248	14.37			
	0.2178	14.55			
	0.9718	14.32			

MEASUREMENT OF LATTICE PARAMETERS

The lattice parameters of the 13 single crystals were measured on a series 3488 Picker diffractometer. On most of the samples data were taken from the (110) face rather than from the (100) face because diffraction peaks of higher values of theta could be obtained this way.

A crystal was mounted on a goniometer with its (110) face oriented approximately such that its normal was midway between the beam and the detector. Two theta was adjusted for approximately the value that would give rise to the (220) reflection. Omega and chi were adjusted to maximize the detector output.

To insure that the center of the diffracting volume was at the center of the diffractometer the following iteration was performed. First, theta was advanced until the highest order line was found. From this value of theta a new value of theta for the lowest order line was calculated. The diffractometer was then set to this calculated value and the crystal was moved in a direction perpendicular to its face until the counter output was again maximized. This process was repeated until no further improvement in diffracted beam intensity could be achieved. This iteration converged rapidly, and generally no more than three iterations were necessary to achieve the desired results. To insure correct adjustment of omega, theta was adjusted to the highest order line and omega

was adjusted to maximize the detector output.

Theta was scanned and the detector output as a function of theta was recorded on a Texas Instrument chart recorder. The value of theta for each diffraction line was determined by measuring the center of the peak at half-height. The lattice parameter for each crystal was obtained from the peak positions by using a double precision version of a weighted least-squares program written by Dr. F. X. Kayser. The results of this program are listed along with the compositions in Table 3. The precision of the values of lattice parameter is estimated to be ± 0.0001 angstroms.

Table 3. The lattice parameters of iron-silicon alloys at 21 degrees Celsius, taken from molybdenum K- α diffraction patterns

Sample	Lattice parameter angstroms	Composition atom percent silicon
1	2.8641	3.61
2	2.8628	5.47
3	2.8588	8.75
4	2.8568	9.46
5	2.8562	10.53
6	2.8551	12.27
7	2.8490	15.59
8	2.8434	17.48
9	2.8390	19.91
10	2.8358	21.62
11	2.8294	24.38
12	2.8294	24.27
13	2.8275	24.85

MEASUREMENT OF RESISTIVITY

The resistivity samples were spark-cut from the same single crystals that were used in the precision lattice parameter determinations. They were in the form of parallelepipeds of approximate dimensions of $1 \times 1 \times 15 \text{ mm}^3$. Opposite faces were lapped to within better than 0.005 mm of being parallel. Tantalum leads, 0.0125 mm in diameter, were cleaned in a 5 percent solution of hydrofluoric acid in water and attached to the specimens by spot-welding. The specimens were given an ordering anneal to remove any disorder that may have been introduced by the lapping, cutting or spot-welding. The distance between the leads was measured with a Gaertner microscope mounted on a Kinamatic micrometer positioner. The error in measuring the distance between the leads was less than 0.05 mm. Samples were mounted on phenolic boards using Mueller 34-C clips.

The direct current electrical resistance of each specimen was measured at room temperature and at 77.4 degrees Kelvin using the standard 4-terminal resistor technique (13,14). The resistance of each specimen was compared to a nominal 0.001 ohm resistor. The value of the latter was determined to be 0.0009997 ± 0.0000005 absolute ohms by calibrating it against a National Bureau of Standards resistor. Potential measurements were made with a Leeds and Northrup K-5 potentiometer. A diagram of the electrical configuration is given in Figure 2.

Figure 2. The electrical configurations used for measuring resistivity

For a given specimen, four resistivity measurements were made at each temperature: two with the current flow in one direction and two with the current flow in the reverse direction. The resistivity was calculated from Equation 1 and the average of the four measurements was reported.

$$\rho = \frac{d_1 d_2 R_s V_u}{\ell V_s} \quad (1)$$

The symbols used in Equation 1 are defined in Table 4.

Table 4. Definition of the symbols used in Equation 1

Symbol	Definition
d_1, d_2	two dimensions of the sample perpendicular to the current flow
ℓ	length between potential leads
R_s	resistance of the standard
ρ	resistivity of the unknown
V_s	voltage measured across standard
V_u	voltage measured across unknown

The values of ρ obtained and the maximum possible error in measurement for each value are given in Table 5. The values of ρ are plotted as a function of composition in Figure 3. The dashed curve in Figure 3 is the room temperature resistivity versus composition curve of Kayser (12). The departures from this curve are an indication of the lack of soundness of the cast samples.

Figure 3. The resistivity of iron-silicon single crystals

Table 5. The resistivity of iron-silicon alloys as a function of composition

Sample number	$\rho(300^\circ\text{K})$	$\rho(77.35^\circ\text{K})$	$\Delta\rho(300^\circ\text{K})$	$\Delta\rho(77.35^\circ\text{K})$
	Micro-ohm-meters			
1	0.35935	0.25725	6.61×10^{-3}	4.84×10^{-3}
2	0.47903	0.38478	7.38×10^{-3}	5.96×10^{-3}
3	0.65825	0.57662	9.48×10^{-3}	8.30×10^{-3}
4	0.68179	0.60741	9.41×10^{-3}	8.38×10^{-3}
5	0.82945	0.74012	11.20×10^{-3}	9.99×10^{-3}
7	0.93750	0.80205	17.06×10^{-3}	14.60×10^{-3}
8	1.04524	0.85067	12.54×10^{-3}	10.21×10^{-3}
10	0.87790	0.56966	12.29×10^{-3}	8.03×10^{-3}
13	0.21917	0.02211	4.48×10^{-3}	0.52×10^{-3}

In addition, the resistivity of the Fe_3Si crystal, sample 13, was measured as a function of temperature. A copper-constantan thermocouple was used to determine the temperature. This thermocouple was mechanically affixed to the center of the sample. The procedure for obtaining two consecutive data points was as follows: (i) the temperature was recorded giving T_1 , (ii) the resistance was measured with the current flow in the forward direction giving R_1 , (iii) the resistance was measured with the current flow in the reversed direction giving R_2 , (iv) the temperature was recorded giving T_2 , (v) the resistance was measured with the current flow in the reversed direction giving R_3 , (vi) the resistance was measured with the current flow in the forward direction giving R_4 , and (vii) the temperature was measured giving T_3 . The values of the data

points were calculated using Equations 2, 3, 4 and 5.

$$R'_1 = (R_1 + R_2)/2 \quad (2)$$

$$R'_2 = (R_3 + R_4)/2 \quad (3)$$

$$T'_1 = (T_1 + T_2)/2 \quad (4)$$

$$T'_2 = (T_2 + T_3)/2 \quad (5)$$

The justification of this outlined technique is given by Equations 6 thru 12, where R'' is the contribution to the resistivity due to electromotive force effects at the leads.

$$R_1 = R(T_1) + R''(T_1) \quad (6)$$

$$R_2 = R(T_2) - R''(T_2) \quad (7)$$

$$R_3 = R(T_2) - R''(T_2) \quad (8)$$

$$R_4 = R(T_3) + R''(T_3) \quad (9)$$

$$R'_1 = \frac{R(T_1) + R(T_2)}{2} + \frac{R''(T_1) - R''(T_2)}{2} \quad (10)$$

$$R'_1 = R\left(\frac{T_1 + T_2}{2}\right) - \frac{\Delta R''}{2} \left(\frac{T_1 + T_2}{2}\right) \quad (11)$$

$$R'_2 = R\left(\frac{T_2 + T_3}{2}\right) + \frac{\Delta R''}{2} \left(\frac{T_2 + T_3}{2}\right) \quad (12)$$

R'_1 is shifted from its true value an amount equal to $\Delta R''/2$ while R'_2 is shifted in the opposite direction by an amount of approximately the same magnitude. When a series of points taken in the described manner is plotted and a best fit curve is drawn through them the deviations from the true value are cancelled out. The value of ρ as a function of temperature

are given in Table 6.

Table 6. The electrical resistivity of Fe_3Si as a function of temperature

Temp. (°K)	ρ ($\mu\Omega\text{-M}$)	Temp. (°K)	ρ ($\mu\Omega\text{-M}$)	Temp. (°K)	ρ ($\mu\Omega\text{-M}$)
4.215	0.0060608	191.0	0.11218	213.0	0.13368
77.35	0.0221114	192.5	0.11354	216.0	0.13710
90.18	0.0284903	194.0	0.11511	219.5	0.13967
179.0	0.10043	196.0	0.11685	221.5	0.14241
181.0	0.10262	197.0	0.11802	223.5	0.14456
182.0	0.10363	198.0	0.11913	227.0	0.14780
183.0	0.10429	199.0	0.12000	228.00	0.14929
184.0	0.10520	200.0	0.12066	231.0	0.15190
185.0	0.10603	201.0	0.12177	239.0	0.16006
186.0	0.10688	203.0	0.12331	241.0	0.16222
187.0	0.10733	205.0	0.12557	273.0	0.19415
188.0	0.10897	207.5	0.12825	296.0	0.21844
189.0	0.10997	209.0	0.12970	332.0	0.25917
190.0	0.11090	210.5	0.13117	372.0	0.30519

STRUCTURAL DETERMINATION

In considering the possible structures of iron-silicon alloys in the composition range of zero to twenty-five atom percent silicon, it is convenient to begin with the DO_3 structure, which is the equilibrium structure of Fe_3Si at room temperature. This structure, the unit cell of which is shown in Figure 4, may be considered to be composed of four interpenetrating face-centered cubic sublattices denoted here as I, II, III, and IV. The unit cell has sixteen atom positions as given in Table 7. Three possibilities arise for the positions of the silicon atoms. They could be (i) randomly distributed over all sites giving the body-centered structure of pure iron, (ii) randomly distributed over only one sublattice giving the DO_3 structure of Fe_3Si , or (iii) randomly distributed over a pair of sublattices like III and IV giving the B2 structure.

The structure factor for the three possibilities are calculated from the general form, for the sixteen atom unit cell, given in Equation 13 where f_I , f_{II} , f_{III} and f_{IV} are the average scattering factors of the corresponding sublattices.

$$F_{hkl} = [1 + \exp[\pi i(h+k)] + \exp[\pi i(h+l)] + \exp[\pi i(k+l)] \\ [f_I + f_{II} \exp[\pi i h] + f_{III} \exp[\frac{1}{2} \pi i(h+k+l)] + \\ f_{IV} \exp[\frac{1}{2} \pi i(3h+k+l)]] \quad (13)$$

Table 7. The positions of the atoms in the DO_3 structure

Sublattice	Coordinates of atom positions in unit cell											
I	0	0	0	1/2	1/2	0	0	1/2	1/2	1/2	0	1/2
II	1/2	0	0	1	1/2	0	1/2	1/2	1/2	1	0	1/2
III	1/4	1/4	1/4	3/4	3/4	1/4	1/4	3/4	3/4	3/4	1/4	3/4
IV	3/4	1/4	1/4	1/4	3/4	1/4	3/4	3/4	3/4	3/4	1/4	1/4

Figure 4. The sixteen atom unit cell

For all cases the structure factor will be zero if the indices are mixed.

For the DO_3 case f_I , f_{II} and f_{III} are equal to $(f_{Fe}r_\alpha + f_{Si}w_\alpha)$ while f_{IV} equals $(f_{Si}r_\beta + f_{Fe}w_\beta)$. r_α and r_β are the probabilities of an iron atom being on an α site and a silicon atom being on a β site respectively, while w_α and w_β are equal to $(1-r_\alpha)$ and $(1-r_\beta)$. The long range order parameter is related to these probabilities by Equation 14. The DO_3 structure

$$S = r_\alpha - w_\beta = r_\beta - w_\alpha \quad (14)$$

factor is given by Equation 15 for non-mixed indices. For the

$$F_{hkl} = 4[(f_{Fe}r_\alpha + f_{Si}w_\alpha)(1 + \exp(\pi h) + \exp(\frac{1}{2}\pi(h+k+l))) + (f_{Si}r_\beta + f_{Fe}w_\beta)(\exp(\frac{1}{2}\pi(3h+k+l)))] \quad (15)$$

case where all the indices are even and the quantity, $(h+k+l)/2$ is also even the structure factor is given by Equation 16, where X_{Fe} is the atom fraction iron and X_{Si} is the atom fraction silicon. These lines are fundamental lines as is shown

$$F_{hkl} = 16[f_{Fe}X_{Fe} + f_{Si}X_{Si}] \quad (16)$$

by the absence of the long range order parameter in the structure factor. For the case where the indices are all even and the quantity, $(h+k+l)/2$, is odd, the structure factor is given by Equation 17. The structure factor for the case where all the indices are odd is also given by Equation 17.

$$F_{hkl} = 4S(f_{Fe} - f_{Si}) \quad (17)$$

The structure factor for the B2 case is calculated from Equation 13 by making the substitutions indicated by Equations 18 and 19. This gives a structure factor which is identical to that of the DO_3 with one exception. When all the indices are odd the structure factor for the B2 is equal to zero. The structure factor for the body-centered cubic case has only one non-zero condition, the fundamental of the other two cases. This structure factor is given by Equation 16.

$$f_I = f_{II} = (f_{\text{Fe}}^r + f_{\text{Si}}^w) \quad (18)$$

$$f_{III} = f_{IV} = (f_{\text{Si}}^r + f_{\text{Fe}}^w) \quad (19)$$

The results of these structure factor calculations for the sixteen atom unit cell are summarized in Table 8. It is obvious from Table 8 that diffraction patterns from both (100) and (111) faces would be necessary in order to determine which of the structures are present. For all samples with the exception of 6, 9, 11 and 12 specimens were prepared with (100) and (111) faces. These specimens were given an ordering-anneal and diffraction patterns were obtained giving the results tabulated in Table 9.

Table 8. The results of the structure factor calculations on the sixteen atom unit cell

Line	BCC	B2	DO ₃
(100)	---	Superlattice	Superlattice
(200)	---	Superlattice	Superlattice
(300)	---	Superlattice	Superlattice
(400)	Fundamental	Fundamental	Fundamental
(111)	---	---	Superlattice
(222)	---	---	Superlattice
(333)	---	---	Superlattice
(444)	Fundamental	Fundamental	Fundamental

Table 9. The observed diffraction peaks for the (100) and (111) faces of iron-silicon single crystals

Sample number	Atom percent silicon	(100) face ^a	(111) face ^a
1	3.61	FO	FO
2	5.47	FO	FO
3	8.75	FO	FO
4	9.46	FO	FO
5	10.53	SL	SL
6	12.27	SL	NA
7	15.59	SL	SL
8	17.48	SL	SL
9	19.91	SL	NA
10	21.62	SL	SL
11	24.38	NA	NA
12	24.27	NA	NA
13	24.85	SL	SL

^aFO represents fundamental line only. SL represents fundamental plus superlattice lines. NA represents a crystal face that was not available for study.

ACOUSTIC MEASUREMENTS

The elastic constants of the Fe_3Si crystal were measured by acoustical techniques. According to Nye (15), the elastic tensor, which is a fourth rank tensor relating the stress to the strain in the elastic region, can be reduced, for the cubic case, from its original 81 components to 3 components. In the reduced matrix notation these terms are labeled C_{11} , C_{12} and C_{44} . From Kittel (16), the relationships between these constants and the velocity of the acoustic wave, propagating in the 110 direction is given by Equations 20, 21 and 22 where ρ is the density of the solid and the velocities are defined as follows: (i) V_1 is the velocity of a shear wave polarized in the 001 direction, (ii) V_2 is the velocity of a shear wave polarized in the $\bar{1}10$ direction and (iii) V_3 is the velocity of a longitudinal wave.

$$V_1^2 \rho = C_{44} \quad (20)$$

$$V_2^2 \rho = (C_{11} - C_{12})/2 = C' \quad (21)$$

$$V_3^2 \rho = (C_{11} + C_{12} + 2C_{44})/2 = C_L \quad (22)$$

The elastic constants were calculated after determining V_1 , V_2 and V_3 . The latter requires a measurement of the transit time T , that is the time for a shear or longitudinal mode acoustic pulse introduced into an oriented crystal to travel through the crystal and return to the face at which it was introduced. The velocity was calculated from Equation 23,

$$V = 2X/T \quad (23)$$

where X is the distance between two parallel faces. The transit time was measured by a method described by Eshelman (17). A description of the electronic system is included in Appendix D.

The Fe_3Si crystal was in the form of a parallelepiped with dimensions given in Table 10. The density of the crystal, as determined from its lattice parameter and chemical composition, is 7.1955 grams/centimeter³. Gold plated 10 Mhz x and y -cut quartz transducers were used to introduce longitudinal and shear waves into the sample. The transducers were bonded to the crystal with Fisher Nonaq stopcock grease.

Table 10. Dimensions and misorientation angles of crystal 5-91-24

Crystallographic face	Dimension meters ($\times 10^{-1}$)	Angular misorientation	
		θ	ϕ
110	0.8538	1.80	84.89
$\bar{1}10$	1.3840	1.34	56.19
001	1.4310	----	-----

The internal consistency of the measurements was evaluated by making measurements on two sets of 110 faces with the crystal at liquid nitrogen temperature. The results of these measurements, corrected for angular misorientation by the method described by Waterman (18) and illustrated in Appendix C, are given in Table 11. The reproducibility for the two

(110) faces, of the order of several tenths of a percent as indicated in Table 11, is satisfactory.

Table 11. The elastic constants of crystal 5-91-24 at 77.35°K for the (110) and ($\bar{1}10$) faces

	(110)	($\bar{1}10$)
C_L	3.4090	3.4059
C'	0.4178	0.4174
C_{44}	1.4021	1.3961

The transit times for the three modes were measured with waves propagating in the 110 direction at liquid helium temperature and as a function of temperature. The temperature, over the range of 77.35 degrees Kelvin to room temperature, was measured with a copper-constantan thermocouple. The constants, C_L , C' and C_{44} , corrected for angular misorientation, are given in Tables 12, 13 and 14. The room temperature points for all three modes were taken in a magnetic field, at practical saturation, to remove the severe signal attenuation effects of the domain walls. The precision of the measurement of the elastic constants is estimated to be better than 0.2 percent. The accuracy of the temperature, as measured by the thermocouple, is estimated to be of the order of 2.0 degrees Kelvin.

The elastic constants were least-squared fitted to the analytical function suggested by Varshni (19). This function

Table 12. C_{44} as a function of temperature

Temp. °K	Newton/meter ² ($\times 10^{-11}$)		
	C_{44} (meas.)	C_{44} (calc.) ^a	ΔC_{44}
4.20	1.4065	1.4059	5.83000D-04
77.35	1.4021	1.4028	-6.54268D-04
118.91	1.3956	1.3961	-5.11267D-04
119.56	1.3956	1.3960	-3.90947D-04
140.27	1.3920	1.3920	1.47312D-05
151.91	1.3899	1.3896	2.86117D-04
162.79	1.3870	1.3873	-3.36976D-04
168.90	1.3856	1.3860	-4.36521D-04
177.42	1.3849	1.3842	6.99711D-04
187.47	1.3828	1.3820	7.95836D-04
191.47	1.3813	1.3811	1.78028D-04
199.40	1.3792	1.3794	-1.60743D-04
200.49	1.3785	1.3791	-6.17457D-04
207.03	1.3778	1.3777	1.47937D-04
214.63	1.3757	1.3759	-2.37741D-04
228.74	1.3736	1.3727	8.73845D-04
234.49	1.3722	1.3714	7.92170D-04
243.32	1.3694	1.3694	2.62479D-05
295.15	1.3562	1.3573	-1.05027D-03

$$^a C_{44} \text{ (calc.)} = 1.4059 - .056348 / [\exp(227/T) - 1].$$

Table 13. C_L as a function of temperature

Temp. °K	Newton/meter ² ($\times 10^{-11}$)		
	C_L (meas.)	C_L (calc.) ^a	ΔC_L
4.20	3.4145	3.4125	1.99800D-03
77.35	3.4090	3.4101	-1.13514D-03
80.34	3.4118	3.4097	2.12677D-03
104.15	3.4035	3.4043	-8.05859D-04
122.82	3.4008	3.3982	2.60972D-03
123.47	3.3953	3.3980	-2.65113D-03
130.63	3.3926	3.3952	-2.61142D-03
144.11	3.3871	3.3896	-2.47280D-03
155.11	3.3844	3.3846	-1.64144D-04
162.58	3.3790	3.3810	-1.98079D-03
174.32	3.3736	3.3751	-1.48744D-03
180.53	3.3709	3.3719	-9.53882D-04
195.50	3.3628	3.3638	-9.70452D-04
199.09	3.3628	3.3618	1.02287D-03
207.33	3.3601	3.3571	2.97010D-03
211.94	3.3547	3.3545	2.11102D-04
217.09	3.3520	3.3515	4.93945D-04
220.91	3.3520	3.3493	2.72749D-03
226.49	3.3493	3.3460	3.32058D-03
233.15	3.3440	3.3420	1.99568D-03
236.51	3.3413	3.3400	1.31855D-03
238.82	3.3386	3.3386	1.57578D-05
248.83	3.3360	3.3325	3.52802D-03
252.15	3.3280	3.3304	-2.42512D-03
273.15	3.3122	3.3173	-5.07672D-03
292.08	3.3069	3.3052	1.73461D-03
292.33	3.3043	3.3050	-7.04001D-04
293.37	3.3017	3.3043	-2.63224D-03

$$^a C_L \text{ (calc.)} = 3.4125 - .26975/[\exp(367/T)-1].$$

Table 14. C' as a function of temperature

Temp. °K	Newton/meter ² (x10 ⁻¹¹)		
	C' (meas.)	C' (calc.) ^a	ΔC'
4.20	0.4191	0.4186	5.42000D-04
77.35	0.4178	0.4178	-4.95336D-05
79.15	0.4177	0.4178	-6.21469D-05
103.89	0.4157	0.4159	-2.19823D-04
117.67	0.4141	0.4144	-2.95351D-04
119.83	0.4140	0.4141	-1.26949D-04
120.19	0.4137	0.4141	-3.81478D-04
145.23	0.4108	0.4104	3.51189D-04
77.35	0.4178	0.4178	-4.95336D-05
80.78	0.4177	0.4177	2.23728D-05
90.76	0.4175	0.4170	4.53446D-04
105.40	0.4163	0.4158	5.30713D-04
111.39	0.4147	0.4151	-4.31398D-04
115.92	0.4141	0.4146	-5.07169D-04
120.60	0.4135	0.4140	-5.29438D-04
159.85	0.4085	0.4080	5.41444D-04
167.76	0.4062	0.4065	-3.17325D-04
172.15	0.4051	0.4057	-5.91919D-04
174.56	0.4046	0.4052	-6.31486D-04
186.49	0.4039	0.4029	1.01861D-03
187.50	0.4032	0.4027	5.22672D-04
189.98	0.4024	0.4022	2.26898D-04
191.76	0.4022	0.4018	3.91528D-04
194.09	0.4014	0.4013	7.21805D-05
212.33	0.3973	0.3974	-1.44230D-04
211.15	0.3979	0.3977	1.98503D-04

$$^a C' \text{ (calc.)} = .41856 - .11329/[\exp(393/T)-1].$$

Table 14. (Continued)

Temp. °K	Newton/meter ² ($\times 10^{-11}$)		
	C' (meas.)	C' (calc.) ^a	$\Delta C'$
212.99	0.3974	0.3973	1.00003D-04
213.49	0.3974	0.3972	2.09431D-04
214.70	0.3972	0.3969	2.74813D-04
215.97	0.3968	0.3966	1.54208D-04
219.40	0.3957	0.3959	-1.86934D-04
221.51	0.3954	0.3954	-1.70930D-05
223.91	0.3949	0.3949	2.00424D-05
224.57	0.3945	0.3947	-2.31748D-04
227.15	0.3940	0.3942	-1.50362D-04
232.15	0.3929	0.3930	-1.14754D-04
233.52	0.3928	0.3927	9.83861D-05
237.64	0.3920	0.3918	2.45044D-04
237.69	0.3916	0.3917	-1.43422D-04
241.64	0.3907	0.3908	-1.28989D-04
242.98	0.3904	0.3905	-1.17323D-04
244.32	0.3900	0.3902	-2.04937D-04
246.26	0.3894	0.3898	-3.51423D-04
295.15	0.3793	0.3779	1.39261D-03

Table 15. The Debye temperature of Fe₃Si

Temperature °K	Debye temperature °K
4.2	501.4
77.35	504.5

is given in Equation 24. The calculated value of the elastic

$$C = C_0 - A/(\text{Exp}(b/T)-1) \quad (24)$$

constants and the residuals of the fitting process are given in Tables 12, 13 and 14. The method used in fitting the data to the analytic function is discussed in Appendix E.

For the liquid nitrogen and helium data points, the value of the Debye temperature was evaluated by the method described by Overton and Schuch (20). The values obtained are listed in Table 15.

DISCUSSION

The lattice parameter versus composition curve for the iron-silicon alloys is shown in Figure 5. The curve is essentially the same as that determined by Kayser (F. X. Kayser, Iowa State University, unpublished data, 1975) with one important difference, the area between 8.5 and 12 atom percent silicon. The curve in Figure 5 shows two distinct areas of inflection. The inflection at approximately 10 atom percent silicon is apparently associated with the change from a disordered solid solution to a long range ordered structure. The Figures 6, 7, 8 and 9 show that the 9.46 atom percent silicon single crystal does not show any evidence of long range order while the 10.53 atom percent silicon crystal shows both a (200) and a (222) long range order peak. The presence of both of these peaks is evidence that long range order of the DO_3 type exists for this composition. The series of Figures 8-15 indicate that the DO_3 structure is present all the way up to and including 25 atom percent silicon. The second inflection in the lattice parameter versus composition curve at approximately 12 atom percent silicon appears to be related to the change in slope of the resistivity versus composition curve shown in Figure 3. This second inflection probably corresponds to the composition where homogeneous long range order, that is long range order throughout the volume, sets in. In the composition range

Figure 5. The lattice parameters of iron-silicon single crystals as determined by x-ray diffraction (Zr filtered Mo K_{α} x-radiation).

Figure 6. Diffractometer trace obtained at room temperature from an Fe-9.46 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation

Figure 7. Diffractometer trace obtained at room temperature from an Fe-9.46 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation

Figure 8. Diffractometer trace obtained at room temperature from an Fe-10.53 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation.

Figure 9. Diffractometer trace obtained at room temperature from an Fe-10.53 at.% Si single crystal; Zr filtered Mo K_α x-radiation

Figure 10. Diffractometer trace obtained at room temperature from an Fe-12.27 at.% Si single crystal; Zr filtered Mo K_α x-radiation

Figure 11. Diffractometer trace obtained at room temperature from an Fe-15.59 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation

Figure 12. Diffraction trace obtained at room temperature from an Fe-17.48 at.% Si single crystal; Zr filtered Mo K_α x-radiation

Figure 13. Diffractometer trace obtained at room temperature from an Fe-17.48 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation

Figure 14. Diffractometer trace obtained at room temperature from an Fe-19.91 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation

Figure 15. Diffractometer trace obtained at room temperature from an Fe-21.62 at.% Si single crystal; Zr filtered Mo K_{α} x-radiation

between the two inflections it is believed that small areas of long range order exist in the disordered matrix.

It is obvious that the apparent critical points in the lattice parameter versus composition curve, Figure 5, and in the resistivity versus composition curve, Figure 3, do not correspond with the phase boundaries as represented in the most recent phase diagram, Figure 1-b, moreover the apparent qualitative agreement with the phase diagram presented by Hansen (7), Figure 1-a, is fortuitous. This is because the boundaries of that phase diagram at room temperature were deduced from lattice parameter versus composition data that are not in agreement with the results of this investigation, nor with those of another investigator (F. X. Kayser, Iowa State University, unpublished data, 1975).

In conclusion this investigation has given a new feature to the lattice parameter versus composition curve. This new feature has pointed out errors in the presently proposed phase diagrams, however it cannot of itself provide detailed information relative to all the aspects of structure in this system. This investigation has underlined the importance of using carefully prepared single crystals, precision lattice parameter techniques as an early step in investigations of order-disorder transformations. The advantage of using single crystals for detecting long range order is apparent from Figure 8.

The directly measured elastic constants, C_L , C' and C_{44} ,

of Fe_3Si , crystal 13, as a function of temperature are given in Figures 16, 17, and 18. The temperature dependence of C_{11} , C_{12} , the bulk modulus and the anisotropy as calculated from the directly measured constants are given in Figures 19, 20, 21 and 22. From the elastic constant curves it is apparent that no phase transition occurs. It is of interest to compare the values of these parameters at fixed temperatures to those of iron (21) and Fe_3Al (22), the latter having the same DO_3 crystal structure. This comparison along with a comparison of Debye temperatures is given in Table 16. The polycrystalline elastic constants calculated by the schemes of Voight and Reuss as presented by Hearmon (23) are also given in Table 16. From the elastic moduli and constants it is obvious that Fe_3Si is much stiffer than both iron and Fe_3Al .

The resistivity of Fe_3Si as a function of temperature is given in Figure 23. This curve also shows no evidence of a phase transition. The low value of resistivity this alloy attains near absolute zero is unusual for an alloy but more typical of a pure material. This low value is indicative of the high degree of order present in this alloy. It also indicates that there are very few domain walls acting as scattering sites in the sample. Normally a value of the Debye temperature could be deduced from the shape of the resistivity versus temperature curve but in this case it cannot because of the magnetic contribution which cannot be accounted for.

Figure 16. C_L of Fe₃Si as a function of temperature plotted with $\pm 0.1\%$ error bars

Figure 17. C' of Fe_3Si as a function of temperature plotted with $\pm 0.1\%$ error bars

Figure 18. C_{44} of Fe₃Si as a function of temperature plotted with $\pm 0.1\%$ error bars

Figure 19. C_{11} of Fe_3Si as a function of temperature

Figure 20. C_{12} of Fe_3Si as a function of temperature

Figure 21. Bulk modulus of Fe₃Si as a function of temperature

Figure 22. Anisotropy of Fe₃Si as a function of temperature

Figure 23. Electrical resistivity of Fe₃Si as a function of temperature

In conclusion the study of the Fe_3Si single crystal has provided data on the resistivity, thermodynamic, and mechanical properties of this material. It has shown that there are no apparent phase transitions below 400 degrees Kelvin.

Table 16. The room temperature values for Fe_3Si , Fe and Fe_3Al of the elastic constants, the elastic moduli and the anisotropy

Property	Fe_3Si	Fe	Fe_3Al
$C_L (\text{N/M}^2 \times 10^{-11})$	3.3017	2.98	2.8250
$C' (\text{N/M}^2 \times 10^{-11})$	0.3793	0.480	0.2019
$C_{44} (\text{N/M}^2 \times 10^{-11})$	1.3562	1.165	1.3170
$B (\text{N/M}^2 \times 10^{-11})$	1.8191	1.64	1.4407
Anisotropy	3.5755	2.427	6.523
$E_V (\text{N/M}^2 \times 10^{-11})$	2.4610	2.26	2.1596
$E_T (\text{N/M}^2 \times 10^{-11})$	1.78547	1.93	1.1244
$G_V (\text{N/M}^2 \times 10^{-11})$	0.96544	0.891	0.86496
$G_T (\text{N/M}^2 \times 10^{-11})$	0.66801	0.740	0.41038
$\theta_D (^\circ\text{K})$	501	472	442

BIBLIOGRAPHY

1. R. M. Bozarth, "Ferromagnetism," D. Van Nostrand Co., New York, N.Y., 1951, Chapter 3.
2. F. Brailsford, "Physical Principles of Magnetism," D. Van Nostrand Co., New York, N.Y., 1966, Chapter 10.
3. J. L. Walter in "The Sorby Centennial Symposium on the History of Metallurgy," C. S. Smith, Ed., Gordon and Breach Science Publishers, New York, N.Y., 1965, pp 517-540.
4. B. D. Cullity, "Introduction to Magnetic Materials," Addison Wesley Publishing Co., Reading, Mass., 1972. Chapter 13.
5. J. E. Hurst and R. V. Riley, Journal of the Iron and Steel Institute, 155, 172 (1947).
6. J. H. Culling in "Metals Handbook," 8th ed., T. Lyman, Ed., American Society for Metals, Metals Park, Ohio, 1961, pp 402-403.
7. M. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Company, Inc., New York, N.Y., 1958, p 713.
8. R. Hultgren, "Selected Values of the Thermodynamic Properties of Binary Alloys," American Society for Metals, Metals Park, Ohio, 1973, pp 871-883.
9. T. G. Chart, High Temperatures-High Pressures, 2, 461 (1970).
10. D. Meinhardt and O. Krisement, Arch. Eisenhüttenw., 36, 293 (1965).
11. S. V. Semenovskaya and D. M. Umidov, Physica Status Solidi (b), 64, 627 (1974).
12. F. X. Kayser, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1963.
13. W. C. Michels, "Electrical Measurements and Their Applications," D. Van Nostrand Co., New York, N.Y., 1957, pp 55-65.
14. G. T. Meaden, "The Electrical Resistance of Metals," Plenum Press, New York, N.Y., 1965, pp 143-158.

15. J. F. Nye, "Physical Properties of Crystals," Oxford, London, 1957, pp 82-168.
16. C. Kittel, "Introduction to Solid State Physics," 4th ed., John Wiley and Sons, Inc., New York, N.Y., 1971, Chapter 4.
17. F. R. Eshelman, USAEC Report IS-2594, Ames, Iowa, Jan. 1972.
18. P. D. Waterman, Phys. Rev., 113, 1240 (1959).
19. Y. P. Varshni, Phys. Rev. B, 2, 3952 (1970).
20. W. C. Overton and A. F. Schuch, USAEC Report LA-3615-MS, Los Alamos, New Mexico, Dec. 1966.
21. A. E. Lord and D. N. Beshers, Journal of Applied Physics 36, 1620 (1965).
22. H. J. Leamy, E. D. Gibson and F. X. Kayser, Acta Metallurgica, 15, 1827 (1967).
23. R. F. S. Hearmon, "Applied Anisotropic Elasticity," Oxford, London, 1961, Chapter 3.
24. H. P. Klug, "X-Ray Diffraction Procedures," John Wiley and Sonc, Inc., New York, N.Y., 1954.

APPENDIX A

It is apparent that the proper alignment of a diffractometer is the first step in obtaining precision lattice parameters. According to Klug (24), "Correct alignment is essential to the attainment of (1) maximum intensity, (2) optimum resolution, and (3) correct angular reading." The procedure used in aligning the Picker diffractometer will be described in some detail.

The reference point from which all adjustments were made is the main axis of the diffractometer. This axis is defined by a 0.625 inch hole in the specimen table. To reference to this hole a tight fitting pin, with a shoulder to rest on the specimen table, was fitted into this hole. Mounted on this pin is a 0.0005 inch lead slit. To insure that the center of the slit was coincident with the main axis of the instrument a light was mounted on one side of the pin while a traveling microscope was mounted on the other side (see Figure A-1). The cross hairs of the microscope were set on the center of the slit, the center pin was then rotated 180 degrees and the distance the slit appeared to move was recorded. The slip was moved one half this distance. This was accomplished by first closing the slit completely by moving one side, and then moving the other side a set distance by using shim stock. This process was repeated until the turning of the alignment pin 180 degrees produced an apparent movement of less than 0.00025.

Figure A-1. Top view of diffractometer showing position of alignment pin

inch.

The next step involved adjusting the diffracted beam collimator support (castle) so that the path through the diffracted beam optical system intersected the main axis. This was done using the system shown in Figure A-2. A pair of slits were mounted on the castle thus forming a collimator. A light was then shined through the collimator and the position of the castle was moved around pivot "A" until the collimated light beam went through the slit on the alignment pin.

The adjustment of the tube position was undertaken next. A slit was mounted on the tube support as shown in Figure A-3. The castle and the alignment pin were rotated about the main axis until the light beam passed through the two slits on the castle, the slit on the alignment pin, and the slit on the tube mount. The light was then removed and a detector was mounted in its place. The take-off angle of the x-ray tube was set to two degrees and the tube was energized. The tube was moved in the $x-x'$ direction shown on Figure A-3 until a maximum detector output was observed. The two theta counter was zeroed and coupled to the diffractometer.

The alignment pin and the first slit on the castle were removed and the take-off angle was set to ten degrees. Theta was scanned and the center of the peak obtained was noted. If the value of theta obtained was positive then the tube was moved in the y direction and if it was negative the tube was

SLITS USED TO
COLLIMATE LIGHT BEAM

Figure A-2. Top view of diffractometer showing slits used to align castle

Figure A-3. Top view of diffractometer showing position of x-ray tube

moved in the y' direction. This process was repeated until the direction of the beam was independent of take-off angle. The alignment pin was then replaced and two theta was again adjusted for a maximum. The counter was reset to zero and the alignment was complete.

APPENDIX B

The following technique was used to determine the mis-orientation of the cut faces of the crystals. A crystal was mounted on the diffractometer and aligned by using a reflection from the crystallographic plane of its face. Omega was then recorded. Once this was done the detector was masked with absorbing material (to prevent damage from the direct beam) and theta was set to zero. Omega was then rocked until a maximum was found. Omega was again recorded. This maximum indicated that the face of the crystal was parallel to the path of the x-ray beam from the tube to the detector. The difference between the two recorded values of omega gives the angle α_1 . The crystal was rotated 90 degrees about an axis perpendicular to the plane under investigation and the procedure was repeated giving α_2 . To convert these into standard polar coordinates the following equations were used.

$$\theta = \text{ARCTAN}[(\tan\alpha_1)^2 + (\tan\alpha_2)^2]^{1/2}$$

$$\phi = \text{ARCTAN}[\tan\alpha_2/\tan\alpha_1]$$

APPENDIX C

To check the calibration and reliability of the pulse echo overlap system of measurement of elastic constants a series of measurements were made on a copper single crystal at room temperature. The crystal had two sets of parallel cut faces which were nominally oriented in the 100 and 011 directions. The angular deviations from correct alignment were measured as described in Appendix B and are given in Table C-1 along with the distance between the faces.

Table C-1. The angular deviation of the copper crystal

Face	θ	ϕ	Dimension
100	1.48°	3.86	1.2935 cm
011	1.32°	36.70	1.7474 cm

The transit times were measured and the results obtained are listed in Table C-2 along with the elastic constants calculated from those times.

Table C-2. The transit times for the copper crystal

Face	Polarization	Time $\mu\text{sec.}$	Elastic constant	C neutron/meter ² $\times 10^{-11}$
011	longitudinal	7.0381	C_L	2.2035
011	01 $\bar{1}$	21.624	C'	0.2335
011	100	12.064	C_{44}	0.7500
100	longitudinal	5.9486	C_{11}	1.6971
100	001	8.928	C_{44}	0.7503

According to Waterman (18) the values of the velocity are altered by misorientation in a manner described by the Equations C-1 thru C-15 in which θ_1 and ϕ_1 represent the misorientation of the 100 face and θ_2 and ϕ_2 are the misorientations of the 011 face. After applying these corrections the values of the corrected elastic constants are given in Table C-3.

$$V_1 = V_2 = \left(\frac{C_{44}}{\rho}\right)^{1/2} \quad (C-1)$$

$$V_3 = (C_{11}/\rho)^{1/2} \quad (C-2)$$

$$V_4 = (C'/\rho)^{1/2} \quad (C-3)$$

$$V_5 = (C_{44}/\rho)^{1/2} \quad (C-4)$$

$$V_6 = (C_L/\rho)^{1/2} \quad (C-5)$$

$$K_1 = C_{11} - C_{12} - 2C_{44} \quad (C-6)$$

$$K_2 = \frac{K_1}{C_{44} - C_{12}} + 2 \quad (C-7)$$

$$K_3 = \frac{K_1}{C_{12} + C_{44}} + \frac{3}{2} \quad (C-8)$$

$$K_4 = \frac{K_1}{2(C_{11} + C_{12})} + \frac{3}{2} \quad (C-9)$$

$$\frac{\Delta V_1}{V_1} = \frac{K_1 \theta_1^2}{4C_{44}} \{K_2 + [K_2^2 - \sin^2 2\phi_1 (2K_2 - 1)]^{1/2}\} \quad (C-10)$$

$$\frac{\Delta V_2}{V_2} = \frac{K_1 \theta_1^2}{4C_{44}} \{K_2 - [K_2^2 - \sin^2 2\phi_1 (2K_2 - 1)]^{1/2}\} \quad (C-11)$$

$$\frac{\Delta V_3}{V_3} = \frac{-K_1 K_2 \theta_1^2}{2C_{11}} \quad (C-12)$$

$$\frac{\Delta V_4}{V_4} = \frac{-K_1 \theta_2^2}{2(C_{11} - C_{12})} [2K_3 \cos^2 \theta_2 + 1] \quad (C-13)$$

$$\frac{\Delta V_5}{V_5} = \frac{K_1 (3 - K_4)}{2C_{44}} \theta_2^2 \sin^2 \theta_2 \quad (C-14)$$

$$\frac{\Delta V_6}{V_6} = \frac{K_1 \theta_2^2}{2(C_{11} + C_{12} + 2C_{44})} [(2K_3 + 1) \cos^2 \theta_2 + (2K_4 - 5) \sin^2 \theta_2] \quad (C-15)$$

Table C-3. The corrected values of the elastic constants of copper

Constant	Face	C Newtons/meter ² x10 ⁻¹¹
C _L	011	2.20375
C'	011	0.232807
C ₄₄	011	0.750285
C ₁₁	011	1.686
C ₁₂	011	1.220
C ₁₁	100	1.6860
C ₄₄	100	0.750259

APPENDIX D

The electronic configuration used in the acoustic measurements is presented in Figure D-1. The bridge oscillator is a General Radio Model 1330-A. The counter is a CMC Model 726-C. The frequency divider is a unit built here at Ames Laboratory from the circuit presented in Figure D-2. The pulse delay generator is a Hewlett Packard Model 222-A. The oscilloscope is a Hewlett Packard Model 180-D. The pulse shaper is a General Radio Model 1217-B. The pulsed oscillator was designed and built at the Instrumentation Shop of Ames Laboratory. A block diagram of the pulsed oscillator is given in Figure D-3.

Figure D-1. Block diagram of system used for ultrasonic measurements

Figure D-3. Block diagram of pulsed oscillator

APPENDIX E

The elastic constants, C_L , C' , and C_{44} , were fitted to the function suggested by Varshni (19) by the following approach. The least-squares process requires that the sum, S , of Equation E-1 be minimized. If one replaces the term, $1/(\exp(B/T_i)-1)$, by Y_i Equation E-2 is formed. Since Equation E-2 is linear it can be solved by linear least-squares

$$S = \sum [C_i^1(\text{meas}) - C_0 + A/(\exp(B/T_i) - 1)]^2 \quad (\text{E-1})$$

$$S = \sum [C_i(\text{meas}) - C_0 + A(Y_i)]^2 \quad (\text{E-2})$$

methods, giving values for both C_0 and A . A value of B was chosen at random, a value of Y_i was formed for each value of T_i and the values of C_0 and A were calculated from Equations E-3 and E-4. The value of B was then incremented by one degree and new values of C_0 and A were calculated. This was done until a minimum in S as a function of B was discovered. The value of B , C_0 and A at this point were reported as parameters of the best least squares fit.

$$C_0 = [(\sum C_i)(\sum Y_i^2) - (\sum Y_i)(\sum Y_i C_i)]/D \quad (\text{E-3})$$

$$A = [N(\sum Y_i C_i) - (\sum Y_i)(\sum C_i)]/D \quad (\text{E-4})$$

$$D = N(\sum Y_i^2) - (\sum Y_i)^2 \quad (\text{E-5})$$