

Fermi-Thomas Method for Crystals*

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A method for solving the Fermi-Thomas and Fermi-Thomas-Dirac equations for crystals is presented. The results of computing the electronic density of copper by this method are given together with those attained from the application of the spherical approximation to the Wigner-Seitz cell. Also presented are the results of cohesive energy calculations for copper, which with the inclusion of the correlation effect predict stability but only about one-third of the observed value.

I. INTRODUCTION

A NUMBER of uses of the Fermi-Thomas and Fermi-Thomas-Dirac statistical models in the study of crystals have been previously suggested, e.g., in providing approximations of the potential field for Schrödinger's equation in the one-electron scheme for deriving crystalline properties, if not in a direct determination of such properties as the cohesive energy, and in giving approximations of the electronic density for comparison with that obtained from x-ray diffraction measurements. The feasibility of this, however, has not been fully explored, presumably because of the difficulty with the corresponding nonlinear differential equations of finding solutions with lattice symmetry.

Slater and Krutter¹ have obtained radial solutions applicable to metals, for which the Wigner-Seitz cell is approximated by a sphere of equal volume. Their results indicated that in this approximation the crystals would be unstable, considering the binding energy as the sum of the changes in the Coulomb, Fermi, and exchange energies accompanying the transition from the crystal to a gas of the free atoms. However, March² has pointed out that the Fermi-Thomas-Dirac model in the spherical approximation does yield a minimum in the curve of energy *vs* lattice spacing, although in the case of copper, which was investigated by Slater and Krutter, the minimum occurs for a lattice spacing beyond the range of their calculations and, therefore, considerably greater than the observed lattice spacing. This he interpreted as affording some explanation of metallic cohesion. For the alkali metals, March showed that this model predicts lattice spacings in fair agreement with observation.

This paper presents a method, which may be applied to polyatomic crystals, for obtaining solutions with lattice symmetry to the Fermi-Thomas and Fermi-Thomas-Dirac equations. The method depends on successive approximations, for whose rapid convergence to the solution an argument is given.

In the case of copper, for which the method was tested, this rapid convergence was borne out. The solu-

tion did not require undue computational labor. The resulting electronic distribution is given, together with that derived from the spherical approximation for comparison. The cohesive energy, computed from the Coulomb, Fermi, exchange, and correlation energies, turns out to be correct in sign but about one-third the measured value. Without the correlation correction the cohesive energy and its components are essentially the same as predicted from the figures provided by Slater and Krutter.

II. MATHEMATICAL DEVELOPMENT

A. Solution of the Fermi-Thomas Equation

Let V_{Z^0} represent the solution for the free atom of the element with atomic number Z to the Fermi-Thomas equation

$$\nabla^2 V = \alpha V^{\frac{3}{2}}, \quad (1)$$

where

$$\alpha = 32\pi^2 e(2me)^{\frac{3}{2}}/3h^3,$$

and $V(\mathbf{r})$ is the potential from the electronic and nuclear charges, plus a constant whose value is not of present concern. The V_{Z^0} , tables of which are readily available,³ are radial functions satisfying the boundary conditions

$$\begin{aligned} rV_{Z^0}(r) &\rightarrow Z \quad \text{as } r \rightarrow 0, \\ V_{Z^0}(r) &\rightarrow 0 \quad \text{as } r \rightarrow \infty, \end{aligned}$$

rendering

$$V_{Z^0}(r) > 0 \quad \text{for } r < \infty. \quad (2)$$

Then, with $V_i(\mathbf{r})$ representing the i th approximation to the solution of Eq. (1) for a crystal, the first approximation may be written

$$V_1(\mathbf{r}) = \sum_Z \sum_{m_Z=1}^{N_Z} V_{Z^0}(|\mathbf{r} - \mathbf{r}_{m_Z}|), \quad (3)$$

where \mathbf{r}_{m_Z} is the center of the m_Z th of the N_Z atoms with atomic number Z in the crystal. Since the V_{Z^0} are solutions of Eq. (1), one has

$$\nabla^2 V_1 = \alpha \sum_Z \sum_{m_Z=1}^{N_Z} [V_{Z^0}(|\mathbf{r} - \mathbf{r}_{m_Z}|)]^{\frac{3}{2}}. \quad (4)$$

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¹ J. C. Slater and H. M. Krutter, *Phys. Rev.* **47**, 559 (1935).

² N. H. March, *Phil. Mag.* **45**, 325 (1954).

³ V. Bush and S. H. Caldwell, *Phys. Rev.* **38**, 1898 (1931).

With a function $q_i(\mathbf{r})$ defined by

$$q_i = \alpha V_i^{\frac{2}{3}} - \nabla^2 V_i, \quad (5)$$

let $v_i(\mathbf{r})$ be the solution of the equation

$$-\nabla^2 v_i + \frac{2}{3}\alpha V_i^{\frac{1}{3}} v_i = q_i \quad (6)$$

that is finite at the nuclear positions and possesses the symmetry of the lattice. Such a solution exists if V_i , and therefore from Eq. (5) q_i , has such symmetry. Defining V_i for $i=2, 3, \dots$ by

$$V_i = V_{i-1} - v_{i-1} \quad (7)$$

gives it this symmetry if V_{i-1} has it. Since V_1 possesses lattice symmetry, by induction it follows that this must be true of V_i for all values of i .

From Eqs. (5) and (6) one obtains

$$\nabla^2(V_i - v_i) = \alpha V_i^{\frac{1}{3}}(V_i - \frac{2}{3}v_i). \quad (8)$$

Now assume that for a particular i , the relations

$$\nabla^2 V_i(\mathbf{r}) > 0, \quad (9a)$$

$$V_i(\mathbf{r}) > 0 \quad (9b)$$

hold. Then from the relations (8) and (9a), and, as a consequence of the lattice periodicity of v_i , the equality

$$\int_c \nabla^2 v_i d\tau = 0, \quad (10)$$

where the integration is over a unit cell, it must follow that

$$0 < \int \nabla^2 V_i d\tau = \alpha \int_c V_i^{\frac{1}{3}}(V_i - \frac{2}{3}v_i) d\tau,$$

which requires that

$$v_i < \frac{2}{3}V_i \quad (11)$$

over at least a portion of the unit cell. Now if there were a region τ_a throughout which $v_i \geq \frac{2}{3}V_i$ and over whose surface S_a $v_i = \frac{2}{3}V_i$, the integration of both sides of Eq. (8) over this region and the application of Gauss's theorem would give

$$\begin{aligned} \frac{1}{3} \int_{\tau_a} \nabla^2 V_i d\tau + \frac{2}{3} \int_{S_a} \nabla_n(V_i - \frac{2}{3}v_i) dS \\ = \alpha \int_{\tau_a} V_i^{\frac{1}{3}}(V_i - \frac{2}{3}v_i) d\tau, \end{aligned}$$

where the second integral on the left would be over this surface S_a . The integrand, the outwardly directed component normal to S_a of the gradient of $V_i - \frac{2}{3}v_i$, would have to be non-negative. This and inequality (9a) would make the sum of integrals on the left positive. Since the integral on the right would be nonpositive, τ_a cannot exist, i.e., relation (11) must hold for all values of \mathbf{r} . This means that under the provisions of

Eqs. (7) and (8), the relations (9a) and (9b) must apply also for $i+1$.

Now these relations are valid for $i=1$, as is evident from inequality (2) and Eqs. (3) and (4). Therefore, by induction one establishes that relations (9a), (9b), and (11) hold for all values of i .

Next assume that for a particular i one has

$$q_i > 0, \quad (12)$$

from which with Eqs. (6) and (10) one obtains

$$0 < \int_c |q_i| d\tau = \frac{2}{3}\alpha \int_c V_i^{\frac{1}{3}} v_i d\tau, \quad (13)$$

indicating that

$$v_i > 0 \quad (14)$$

within at least a portion of the unit cell. Now if there were a region τ_b throughout which $v_i \leq 0$ and over whose surface S_b $v_i = 0$, the integration of both sides of Eq. (6) over this region and the application of Gauss's theorem would yield

$$\int_{S_b} \nabla_n v_i dS = - \int_{\tau_b} (|q_i| - \frac{2}{3}\alpha V_i^{\frac{1}{3}} v_i) d\tau.$$

The integrand on the left, the outwardly directed component normal to S_b of the gradient of v_i , would have to be non-negative. Since the quantity on the right would be negative, the region τ_b cannot exist. Thus, inequality (14) holds for condition (12).

Now from Eqs. (5), (6), and (7), there follows

$$q_{i+1} = \alpha[(V_i - v_i)^{\frac{2}{3}} - V_i^{\frac{2}{3}} + \frac{2}{3}\alpha V_i^{\frac{1}{3}} v_i], \quad (15)$$

from which it may be inferred that under conditions (11) and (14) $q_{i+1} > 0$. Inequality (12) applies for $i=1$, as may be seen from relations (2), (3), (4), and (5) and the fact that

$$(a+b+\dots)^p > a^p + b^p + \dots$$

for

$$a, b, \dots > 0 \quad \text{and} \quad p > 1.$$

Therefore, by induction one proves inequality (12), and as a consequence inequality (14), for all values of i .

One deduces from relations (7) and (9b) that

$$v_1 + v_2 + \dots + v_i < V_1,$$

i.e., the series of positive functions on the left is bounded for all values of i . Consequently, the series converges. Also, from Eq. (15) it follows that $q_i \rightarrow 0$ as $i \rightarrow \infty$ since $v_i \rightarrow 0$ as $i \rightarrow \infty$. Therefore, the sequence V_1, V_2, \dots converges to the solution of Eq. (1).

As an indication of the rapidity of convergence, one may obtain the expression

$$\int_c |q_{i+1}| d\tau < (1/3^i) \int_c |q_i| d\tau$$

from the relations (11), (13), and

$$|q_{i+1}| < (3^{1/2}/4)\alpha(v_i^2/V_i^{1/2}),$$

which follows from expressions (11), (14), and (15) and the fact that

$$(3^{1/2}/4)u^2 > (1-u)^3 - 1 + (3/2)u > 0 \quad \text{for } 0 < u < 2/3.$$

Thus the solution with lattice symmetry to the Fermi-Thomas equation may be developed from the function V_1 , which results from the superposition of the potentials from the atoms of the crystal treated as free, by solving the linear Eq. (6).

B. Solution of the Fermi-Thomas-Dirac Equation

A similar method is proposed for solving for a crystal the Fermi-Thomas-Dirac equation

$$\nabla^2 V = \alpha[(V + \beta^2)^{1/2} + \beta]^3,$$

where $\beta = (2me^3/h^2)^{1/2}$. Again, for the i th approximation one has

$$V_i = V_{i-1} - v_{i-1}, \quad i = 2, 3, 4, \dots,$$

where $V_1 + \beta^2$ may be set equal to the solution of the Fermi-Thomas equation discussed above, and v_i is the solution with lattice symmetry and finiteness at the nuclear positions to the equation

$$-\nabla^2 v_i + \frac{3}{2}\alpha\{[(V_i + \beta^2)^{1/2} + \beta]^2 / (V_i + \beta^2)^{1/2}\}v_i = -\nabla^2 V_i + \alpha[(V_i + \beta^2)^{1/2} + \beta]^3.$$

However, an argument for convergence, analogous to that given in Part A, breaks down at the i th approximation if for some value of \mathbf{r} one finds $V_i < 3\beta^2$.

III. APPLICATION OF THE FERMI-THOMAS METHOD TO COPPER

The condition of lattice periodicity on the solution to Eq. (6) suggests its expression as a Fourier series:

$$v_j = \sum_{\mathbf{k}} a_{\mathbf{k}}^{(j)} \exp(2\pi i \mathbf{k} \cdot \mathbf{r}),$$

$$\mathbf{k} = \sum_{i=1}^3 n_i \mathbf{b}_i,$$

where the \mathbf{b}_i are fundamental translational vectors of the reciprocal lattice and the n_i are integers. Application of the additional condition on v_j , that it transform into itself under the symmetry operations of the point group of the crystal, permits a modification of this expression with a decrease in the number of coefficients to be determined from Eq. (6). For copper, with the Cartesian coordinate axes parallel to the edges of a face-centered cube of the lattice and the origin at the position of one of the nuclei, the center of the Wigner-Seitz cell mentioned below, this expression becomes

$$\sum_{n=m}^{\infty} \sum_{m=l}^{\infty} \sum_{l=0}^{\infty} a_{nml}^{(j)} \sum_{i=1}^6 P_i \cos(2\pi nx/a) \times \cos(2\pi my/a) \cos(2\pi lz/a),$$

where a is the lattice constant, the operator P_i effects the i th of the six permutations on n , m , and l , and $a_{nml}^{(j)}$ vanishes if n , m , and l are neither all even nor all odd.

However, as exemplified by copper, q_1 and $V_1^{1/2}$ vary gradually over the Wigner-Seitz cell except near the nucleus, where they behave according to

$$q_1 = (b/r^3) + c + \dots,$$

$$V_1 = Ze[(1/r) + (128Z/9\pi^2)^{1/2}(B/a_h) + \dots],$$

where a_h is the radius of the first Bohr orbit for hydrogen and the constant B is altered from the free atomic value³ $B_0 = -1.589$. These circumstances recommended the determination of v_1 in two parts, letting $v_1 = v_1' + v_1^{(r)}$.

For the first part, v_1' was represented by the above series with the coefficients other than $a_{000}^{(1)}$, $a_{111}^{(1)}$, $a_{200}^{(1)}$, $a_{220}^{(1)}$, $a_{311}^{(1)}$, and $a_{222}^{(1)}$ set equal to zero. The values for these six coefficients that make v_1' an approximate solution of Eq. (6), i.e., the values that make the corresponding six terms of the Fourier expansion of one side the same as those of the other, were computed. The function q_1' , defined by

$$-\nabla^2 v_1' + \frac{3}{2}\alpha V_1^{1/2} v_1' = q_1',$$

proved to be a close approximation to q_1 except near the nucleus.

For the second part, $v_1^{(r)}$ was obtained as the radial function which, under the boundary conditions that it be finite at $r=0$ and vanish as $r \rightarrow \infty$, satisfies the equation

$$-\nabla^2 v_1^{(r)} + \frac{3}{2}\alpha V_r^{1/2} v_1^{(r)} = q_r,$$

where V_r represents the spherically symmetric approximation of V_1 —although to the three significant figures of the computation, V_1 was radial in the region where $v_1^{(r)}$ was found to be appreciable—and q_r is equal to the spherically symmetric part of $q_1 - q_1'$ in the neighborhood of the nucleus and is zero beyond. The success of this procedure rests upon the fact that $v_1^{(r)}$ became negligibly small while yet well within the Wigner-Seitz cell.

The expression for $q_2(\mathbf{r})$ was accordingly altered from Eq. (15) to

$$q_2 = \alpha[(V_1 - v_1)^{1/2} - V_1^{1/2} + \frac{3}{2}V_1^{1/2}v_1 + \frac{3}{2}(V_r^{1/2} - V_1^{1/2})v_1^{(r)}] + (q_1 - q_1' - q_r).$$

Since the calculated $q_2/\nabla^2 V_2$ nowhere exceeded 1.2%, the second approximation was considered adequate.

The corresponding electronic density n , which from Poisson's equation is equal to $(1/4\pi e)\nabla^2 V_2$ for $r \neq 0$, and V , given as $(\nabla^2 V_2/\alpha)^{1/2}$ rather than V_2 since it is supposed that in a succeeding approximation the latter would undergo the larger percent correction, are presented in Table I. Also given, for comparison, is the spherically approximate electronic density n_s together

with the related quantity V_s , the solution to the Fermi-Thomas equation applicable to copper according to the method of Slater and Krutter. In the neighborhood of the nucleus, n and n_s as well as V and V_s become indistinguishable. For V_2 and V_s the value of the constant B is $B_0+0.00022$.

The table gives the values of these quantities at selected points designated by (N, M, L) in a coordinate system in which the fundamental translation vectors appear as $(20, 20, 0)$, $(20, 0, 20)$, and $(0, 20, 20)$. The point $(0, 0, 0)$ is occupied by a nucleus. The collection of points into which these selected points transform under the operations of the point group of the crystal constitutes a miniature simple cubic lattice that covers the Wigner-Seitz cell.

The numerical integrations over the Wigner-Seitz cell implicit in the formation of the six linear equations in the $a_{nml}^{(1)}$ for determining v_1' were performed by multiplying the value of the integrand at each of the selected points by a weighting factor and summing the products. The weighting factor is proportional to the number of points into which the given selected point is transformed under the operations of the point group.

The contributions to V_1 and $\nabla^2 V_1$ from the free atom centered at $(0, 0, 0)$ and from its nearest neighbors were calculated for each of the selected points. For the next 66 atoms nearest the origin, however, the contributions were computed only at the origin and at points of symmetry, where such computations require less labor, and from these data there were constructed power series approximations in N, M , and L . The remaining atomic centers were treated as though they were distributed continuously with a density of $4/a^3$ over the remaining volume of the crystal. This permitted the formation of expressions in $N^2+M^2+L^2$ for the contributions of these atoms to V_1 and $\nabla^2 V_1$ by integrating $(4/a^3)V_z^0$ and $\alpha(4/a^3)(V_z^0)^{\frac{3}{2}}$, where V_z^0 is assumed to be centered at (N, M, L) , over this volume.

IV. COHESIVE ENERGY OF COPPER

The Fermi and Coulomb, exchange, and correlation contributions to the cohesive energy were calculated from

$$E_{\text{FC}} = \frac{Ze}{2} \lim_{r \rightarrow 0} [V_z^0(r) - V_2(\mathbf{r})] + \frac{e}{10} \left[\int n_0 V_z^0 d\tau - \int n V_2 d\tau \right],$$

$$E_{\text{ex}} = -\frac{3e^2}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{2}} \left[\int n_0^{4/3} d\tau - \int n^{4/3} d\tau \right],$$

$$E_{\text{cor}} = -0.709e^2 \left[\int n_0^{4/3} (1 + 12.6a_n n_0^{\frac{1}{3}})^{-1} d\tau - \int n^{4/3} (1 + 12.6a_n n^{\frac{1}{3}})^{-1} d\tau \right],$$

TABLE I. The electronic distribution and potential in copper from the Fermi-Thomas model.

Selected points <i>N M L</i>			Electronic density (10^{21} cm^{-3})		Potential (volts)	
			With lattice symmetry <i>n</i>	With spherical symmetry <i>n_s</i>	With lattice symmetry <i>V</i>	With spherical symmetry <i>V_s</i>
1	1	1	170	169	1122	1117
3	1	1	29.5	29.4	349	348
5	1	1	7.37	7.32	138	138
7	1	1	2.54	2.54	68.0	68.0
9	1	1	1.13	1.13	39.6	39.6
11	1	1	0.621	0.644	26.6	27.2
13	1	1	0.413	0.438	20.3	21.1
15	1	1	0.325	0.377	17.3	19.1
17	1	1	0.288		15.9	
19	1	1	0.272		15.3	
3	3	1	12.9	12.8	201	200
5	3	1	4.81	4.79	104	104
7	3	1	2.00	1.99	58.0	57.7
9	3	1	0.979	0.977	36.0	36.0
11	3	1	0.579	0.580	25.4	25.4
13	3	1	0.405	0.422	20.0	20.6
15	3	1	0.331	0.375	17.5	19.0
17	3	1	0.299		16.3	
5	5	1	2.54	2.54	68.0	68.0
7	5	1	1.35	1.33	44.5	44.2
9	5	1	0.775	0.763	30.8	30.5
11	5	1	0.516	0.507	23.5	23.2
13	5	1	0.399	0.399	19.8	19.8
15	5	1	0.350		18.1	
7	7	1	0.873	0.857	33.4	33.0
9	7	1	0.605	0.580	26.1	25.4
11	7	1	0.466	0.438	22.0	21.1
13	7	1	0.408	0.380	20.1	19.2
9	9	1	0.497	0.457	22.9	21.7
11	9	1	0.453	0.391	21.5	19.5
3	3	3	7.37	7.32	138	138
5	3	3	3.40	3.38	82.6	82.3
7	3	3	1.62	1.61	50.3	50.1
9	3	3	0.864	0.857	33.1	33.0
11	3	3	0.541	0.540	24.2	24.2
13	3	3	0.396	0.409	19.7	20.1
15	3	3	0.334	0.374	17.6	19.0
17	3	3	0.309		16.7	
5	5	3	2.00	1.99	58.0	57.7
7	5	3	1.14	1.13	39.8	39.6
9	5	3	0.700	0.690	28.8	28.5
11	5	3	0.488	0.479	22.6	22.4
13	5	3	0.389	0.391	19.5	19.5
15	5	3	0.350		18.1	
7	7	3	0.779	0.763	30.9	30.5
9	7	3	0.559	0.540	24.8	24.2
11	7	3	0.445	0.422	21.3	20.6
13	7	3	0.397	0.377	19.7	19.1
9	9	3	0.469	0.438	22.0	21.1
11	9	3	0.431	0.381	20.8	19.2
5	5	5	1.35	1.33	44.5	44.2
7	5	5	0.868	0.857	33.2	33.0
9	5	5	0.592	0.580	25.8	25.4
11	5	5	0.445	0.438	21.3	21.1
13	5	5	0.379	0.380	19.1	19.2
15	5	5	0.357		18.4	
7	7	5	0.640	0.644	27.1	27.2
9	7	5	0.493	0.479	22.8	22.4
11	7	5	0.413	0.399	20.3	19.8
13	7	5	0.381	0.374	19.2	19.0
9	9	5	0.427	0.409	20.7	20.1
11	9	5	0.401	0.377	19.9	19.1
7	7	7	0.517	0.507	23.5	23.2
9	7	7	0.427	0.422	20.7	20.6
11	7	7	0.383	0.380	19.3	19.2
13	7	7	0.374		19.0	
9	9	7	0.385	0.381	19.3	19.2
11	9	7	0.373		18.9	
9	9	9	0.361	0.374	18.5	19.0
11	9	9	0.357		18.4	

where $\mathbf{r}=0$ designates the position of a nucleus, and the integrations involving n_0 , the free atomic electronic density obtained from V_Z^0 , are over all of space. The Fermi part of E_{FC} is derived with the aid of Eq. (1) from the expression $(3h^2/10m)(3n/8\pi)^{3/2}$ for the average kinetic energy of the electrons comprising a Fermi-Dirac gas of density n at absolute zero temperature. The formula for E_{ex} is derived from the expression⁴ $-(3e^2/4)(3n/\pi)^{3/2}$ for the mean exchange energy of such a group of electrons; the formula for E_{cor} , from the Wigner relation⁵ $-0.44e^2/[(3/4\pi n)^{3/2}+7.8a_h]$ for the correlation energy per electron.

The results in Rydberg units are

$$E_{\text{FC}} = -1.63$$

$$E_{\text{ex}} = 1.62,$$

$$E_{\text{cor}} = 0.088,$$

$$\text{Sum} = \text{cohesive energy} = 0.08.$$

Thus with both the exchange and correlation effects considered, the cohesive energy based on charge distributions determined from Fermi-Thomas models for both metallic and isolated atoms falls quite short of the observed value for copper, 0.26 Rydberg unit. On the other hand, March,² using for the metallic atom the minimum energy obtainable from the Fermi-Thomas-Dirac model in the spherical approximation (which does not correspond to the observed lattice spacing), and for the isolated atom the energy, including exchange, derived from a modification of the Fermi-Thomas charge distribution, has computed a value for the cohesive energy of copper that, even with the exclusion of the correlation energy, is too large.

⁴ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 341.

⁵ D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 375.

Superfluid Helium inside Neutron-Irradiated Silicon*

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The specific heat of a boron-doped silicon crystal, which was first irradiated with thermal neutrons and then annealed, showed a pronounced peak at the normal λ temperature of liquid helium. The anomaly is due to the existence of helium inside the ingot, this helium being created by the boron-neutron reaction $\text{B}^{10} + n^1 \rightarrow \text{He}^4 + \text{Li}^7$. On annealing, sufficient helium collected in macroscopic defects within the crystal to liquefy and produce the observed specific heat.

INTRODUCTION

RECENTLY the specific heat of several impure silicon samples has been measured in the liquid helium temperature region. From the electronic contribution to the specific heat information can be obtained concerning the effective mass of the carriers and the energy band structure of the crystal. While we hope to present the results of these measurements in the near future, a very pronounced anomaly was observed in the specific heat of one sample, the explanation of which appears worthwhile to communicate here.

EXPERIMENT

The specific heat of a 92-gram single crystal of silicon containing 0.1% boron has been measured between 1.2°K and 4.2°K using the normal isothermal method (1) when the crystal was in its original state as grown, (2) after irradiation with a flux of 8.5×10^{18} neutrons/cm², and (3) after subsequent annealing in vacuum at 930°C for 24 hours.

Representative results are shown in Fig. 1, where C/T is plotted against T^2 . The specific heat of pure silicon is similar to that of insulators since at low temperatures only a lattice contribution proportional to T^3 is present. However, being heavily doped with boron, this ingot contained a high carrier concentration (holes) before bombardment. Thus, an additional contribution due to the free carriers was found in the specific heat. This contribution, proportional to T , is indicated by the intercept on the C/T coordinate. Irradiation reduced the electronic specific heat practically to zero as most of the free carriers were removed by trapping.

On the basis of the results of Hall coefficient measurements annealing was expected to restore the original hole concentration and, therefore, the original electronic specific heat. This appears to have occurred, but in addition a pronounced peak just at the normal λ point of liquid helium was observed. This temperature coincidence suggested very strongly that liquid helium was responsible for the anomaly. Other possibilities, however, have been investigated.

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