remarkably reduced. One example is given in Fig. 3. For the results of measurements of critical current and field characteristics there exists as yet no well-defined theoretical relationship. A possible explanation would be as follows. Suppose one filament in the weakest part of the superconducting sample has a certain cross section and has maximum current density; because of the compression, which reduces the value of this cross section, the current becomes supercritical. This has the effect that normal conductivity sets in at lower critical current values.

V. CONCLUSION

It seems worthwhile to investigate the pressure dependence of critical temperature, critical current, and critical field in smaller pressure steps up to very high pressures for clean, homogeneous specimens. This would result in a more detailed knowledge of the intrinsic properties of high-field superconductors.

ACKNOWLEDGMENTS

We would like to thank the Deutsche Forschungsgemeinschaft for support of this work.

Discussion 14

B. T. MATTHIAS, *University of California:* The change of T_c with pressure of Nb_3Sn as reported in JETP gives values that are smaller than yours by a factor of 2 from what I remember.

C. MÜLLER, *University of Giessen:* This would be in accordance with what I just mentioned. Our Nb_3Sn values are very much out of line, and perhaps there is something wrong in the whole structure we don't know about yet.

GERHART K. GAULÉ, *U. S. Army Electronics Research and Development Laboratory:* You mentioned in the abstract and you said here that the soft superconductors behave differently from those which you have investigated, by a factor of 2. I pointed out this morning the parameter for a fair comparison should be the atomic volume and not the pressure. Considering that your materials are much harder, I think that you get lesser volume change. If you plot atomic volume vs critical temperature you might find a better agreement.

THERMAL PROPERTIES

CHAIRMAN: *K. Mendelssohn*

Magnetic and Thermal Properties of Second-Kind Superconductors. I. Magnetization Curves*,†

T. KINSEL,‡ E. A. LYNTON, and B. SERIN

Rutgers, The State University, New Brunswick, New Jersey

INTRODUCTION

We have measured, as a function of temperature, the magnetization curves of specimens which formed a group of solid solutions of bismuth in indium. The nominal concentrations ranged from 1.5 to 4.0 at.%. Each sample except the most dilute one was a superconductor of the second kind at its transition temperature T_c. This set of alloys has values of T_c in the liquid-helium temperature range, so that we were able to make a detailed comparison of our results with the predictions of the Ginzburg–Landau–Abrikosov (GLA) theory[1,2] which is derived to be valid near T_c.

The specimens were in the form of long, thin

* This work has been supported by The National Science Foundation and the Rutgers University Research Council.

† Based in part on a dissertation submitted by T.K. to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree.

‡ Socony-Mobil Fellow, 1961–63. Present address: Bell Telephone Laboratories, Whippany, New Jersey.

[1] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950). Cf. also V. L. Ginzburg, Nuovo Cimento **2**, 1234 (1955).

[2] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957) and J. Phys. Chem. Solids **2**, 199 (1957)].

cylinders, and the magnetization was determined with the applied field parallel to the cylinder axes. The measurements were carried out with a vibrating sample magnetometer[3] in conjunction with a niobium solenoid. Details of the experimental procedure and results have been given by Kinsel.[4]

The excellent agreement between theory and experiment near T_c has been reported elsewhere.[5,6] It can be summarized by saying that the values of the Ginzburg–Landau parameter κ, as calculated for each specimen using the Gor'kov–Goodman[7,8] equation[9]

$$\kappa = \kappa_0 + 7.5 \times 10^3 \gamma^{\frac{1}{2}} \rho \,, \tag{1}$$

differ by no more than a few percent from the values of κ obtained from different features of the magnetization curves using the pertinent equations of Abrikosov.[2] These results are listed in Table I.

TABLE I. Summary of results at $t \equiv T/T_c = 1$. κ_1 is obtained from the ratio H_{c2}/H_c, κ_2 from H_{c2}/H_{c1}, and κ_3 from the slope of the magnetization curves near H_{c2} (cf. Ref. 5). κ_4 is calculated from Eq. (1). $\Delta\kappa/\kappa$ gives the maximum percentage deviation of any of the κ values from the average κ value for a particular specimen. Also tabulated are the transition temperatures, T_c, and $\rho_r \equiv R_{4.2°K}/(R_{273°K} - R_{4.2°K})$, where R_T is the specimen resistance at temperature T.

At. % Bi	ρ_r	T_c (°K)	κ_1	κ_2	κ_3	κ_4	$\Delta\kappa/\kappa$ (%)
1.55	0.339	3.76	0.76	0.77	0.76	0.74	2.6
1.70	0.393	3.81	0.88	0.90	0.86	0.85	3.0
1.80	0.419	3.84	0.91	0.95	0.91	0.88	3.8
1.89	0.428	3.88	0.90	0.94	0.90	0.93	2.7
1.95	0.480	3.91	1.05	1.07	1.06	1.03	1.9
2.00	0.530	4.00	1.10	1.14	1.08	1.15	3.6
2.50	0.591	4.10	1.25	1.26	1.22	1.29	3.2
4.00	0.708	4.22	1.46	1.49	1.48	1.53	2.7

At this time we mention and discuss further results which have not been emphasized earlier, and which have particular pertinence to a number of other contributions to this conference.

[3] S. Foner, Rev. Sci. Instr. **30**, 548 (1959).
[4] T. Kinsel, Ph.D. dissertation, Rutgers University, 1963 (unpublished).
[5] T. Kinsel, E. A. Lynton, and B. Serin, Phys. Letters **3**, 30 (1962).
[6] T. Kinsel, E. A. Lynton, and B. Serin, Bull. Am. Phys. Soc. **8**, 294 (1963).
[7] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **10**, 998 (1960)].
[8] B. B. Goodman, IBM J. Res. Develop. **6**, 63 (1961).
[9] $\kappa_0 = 0.112$ is the value of the parameter for pure indium [T. E. Faber, Proc. Roy. Soc. (London) **A241**, 531 (1957)]; γ the Sommerfield electronic specific heat constant in erg cm^{-3} deg^{-2}, and ρ the residual resistivity in in Ω-cm. The values of γ for the alloy specimens were derived from the values of the thermodynamic critical fields in the limit of very low temperatures (cf. Ref. 4). The values of κ obtained in this way differed by at most 5% from those which would be calculated using the value for pure indium.

TEMPERATURE DEPENDENCE OF THE CRITICAL FIELDS

For each specimen the magnetization curve at a given temperature determined the three critical fields: H_{c1}, the lower critical field at which in increasing magnetic fields flux begins to penetrate into the specimen; H_{c2}, the upper critical field at which the sample becomes normal; and H_c, the thermodynamic critical field. As mentioned in Ref. 5, H_{c2} and H_{c1} were obtained by ignoring the slight rounding and tailing of the magnetization curves. The thermodynamic field was calculated by setting the area under each magnetization curve equal to $VH^2/8\pi$, assuming that the initial slope corresponds to a susceptibility of $-1/4\pi$.

Our results for the In–4.0 at.% Bi sample are shown in Fig. 1, in which the three fields are plotted

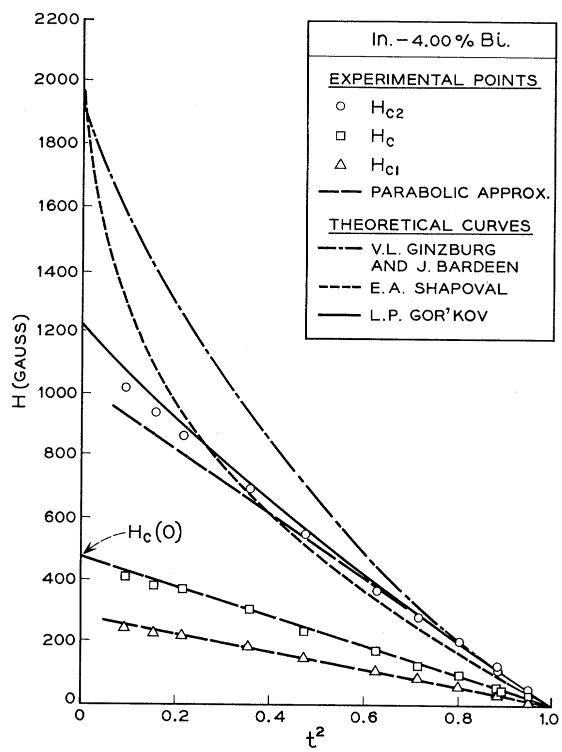

FIG. 1. Temperature dependence of the three critical fields for a typical In–4 at. % Bi sample. The field values are plotted against the square of the reduced temperature $t \equiv T/T_c$, and are compared with parabolic variations as well as with different theoretical predictions for $H_{c2}(t)$.

against the square of the reduced temperature $t \equiv T/T_c$. All qualitative features shown here were also found with all other samples with concentrations of at least 1.55 at.% Bi. As expected, $H_c(t)$ varies very nearly as $H_c(0) \cdot (1 - t^2)$, where $H_c(0)$ is the thermodynamic critical field at $t = 0$. The temperature variation of $H_{c1}(t)$ is about the same. However, our detailed results show that the ratio $h_1(t) \equiv H_{c1}(t)/H_c(t)$ decreases linearly by about 10% over the temperature range between $t = 1.0$ and $t = 0.3$. This is in good agreement with Abrikosov's equation[2] for h_1 as evaluated by Harden and Arp.[10] According to this calculation h_1 should vary for low κ values approximately as $\kappa^{-\frac{1}{2}}$. We presently show that κ increases by about 20% over the temperature range in question, which is thus consistent with a 10% decrease in h_1.

$H_{c2}(t)$, however, increases appreciably more rapidly than $H_c(t)$. Before the development of the microscopic theory of superconductivity,[11] both Bardeen[12] and Ginzburg[13] attempted to extend the Ginzburg–Landau formulation to temperatures below T_c by phenomenological choices for the coefficient in the expansion of the free energy. Both obtain the same temperature dependence

$$H_{c2}(t) = 2\sqrt{2}\kappa(1)H_c(0)[(1 - t^2)/(1 + t^2)]\,, \quad (2)$$

where $\kappa(1)$ is the value of κ at $t = 1$.

Gor'kov,[14] as well as Shapoval,[15] has calculated the temperature variation of $H_{c2}(t)$ from first principles, using Gor'kov's formulation of the BCS theory in terms of Green's functions.[16] Gor'kov's calculations lead to the expression

$$H_{c2}(t) = \kappa(1)H_c(0)(1.77 - 2.20t^2 + 0.50t^4 - 0.07t^6)\,, \quad (3)$$

while Shapoval obtains

$$H_{c2}(t) = 3.03\,\kappa(1)H_{c2}(0)g(t)\,, \quad (4)$$

where $g(t)$ is shown graphically[15] as varying between $g(1) = 0$ and $g(0) = 1$.

The different theoretical predictions for $H_{c2}(t)$ are shown on Fig. 1 by appropriately labeled curves. The experimental results fall somewhat below Gor'kov's prediction, but do approach these quite closely, while the disagreement with Shapoval and with the phenomenological extension of Bardeen and of Ginzburg is quite marked. The disagreement with Shapoval is rather puzzling. Gor'kov started his calculation of $H_{c2}(t)$ with equations which do not take into explicit account the interaction of the electrons with impurities. Shapoval, on the other hand, did allow for this by using instead the equations and the general method of solution which Gor'kov had used on another occasion[7] to calculate successfully other properties of alloy superconductors. It is, therefore, not clear why for our alloys as well as those of others[17,18] $H_{c2}(t)$ should follow Eq. (3) rather than (4).

[10] J. L. Harden and V. Arp, Cryogenics **4**, 105 (1963).
[11] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[12] J. Bardeen, Phys. Rev. **95**, 554 (1954).
[13] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **30**, 593 (1956) [English transl.: Soviet Phys.—JETP **3**, 621 (1956)]; Dokl. Akad. Nauk SSSR **110**, 368 (1956) [English transl.: Soviet Phys.—Dokl. **1**, 541 (1956)].
[14] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].
[15] E. A. Shapoval, Zh. Eksperim. i Teor. Fiz. **41**, 877 (1961) [English transl.: Soviet Phys.—JETP **14**, 628 (1962)].
[16] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].

TEMPERATURE DEPENDENCE OF κ

As pointed out by Berlincourt and Hake,[17] the relationship of the experimental results to the theories is displayed more clearly by defining a temperature-dependent Ginzburg–Landau parameter

$$\kappa(t) \equiv a(t)\kappa(1)\,, \quad (5)$$

such that

$$H_{c2}(t) \equiv \sqrt{2}\,\kappa(t)H_c(t) \quad (6)$$

at all temperatures. With a parabolic temperature variation of $H_c(t)$, the theories predict the following forms for $a(t)$:

Bardeen–Ginzburg: $a(t) = 2/(1 + t^2)$; (7)

Gor'kov: $a(t) = 1.25 - 0.30t^2 + 0.05t^4$; (8)

Shapoval: A nonanalytic form varying from $a(1) = 1$ to $a(0) = 2.14$.

These three forms of $a(t)$ are displayed in Fig. 2, together with the values of $a(t)$ obtained from three of our specimens using Eqs. (5) and (6). Again it is evident that our results are in good agreement with Gor'kov's calculations, except for a systematic deviation to lower values. We see that κ increases by about 23% between $t = 1$ and $t = 0$.

Plotted also in Fig. 2 are values of $a(t)$ obtained for the same three samples from the slopes of their magnetization curves and from the ratio $H_{c2}(t)/H_{c1}(t)$. In making the calculations we assumed that the pertinent Abrikosov relations[2] continue to hold at any temperature with the appropriately adjusted $\kappa(t)$. The close internal agreement in all cases of the three values of $a(t)$ obtained for a given sample at a given temperature indicate strongly that one can indeed apply GLA to a superconductor of the second kind at any temperature by using the appropriate temperature-dependent value of κ.

[17] T. G. Berlincourt and R. R. Hake, Phys. Rev. **131**, 140 (1963).
[18] C. K. Jones, B. S. Chandrasekhar, and J. K. Hulm, Rev. Mod. Phys. **36**, 74 (1964).

Each magnetization curve was taken after the sample had been cooled from above T_c in the absence of an external magnetic field. In calculating H_c, we assume that the curve obtained in this way represents the true reversible magnetization curve, except for the slight rounding at H_{c1} and the small tail at H_{c2}. We found that, for applied fields less than H_{c1}, the magnetization can indeed be varied reversibly. However, on lowering the field again, once this field is exceeded the magnetic moment is always less than in increasing magnetic field. It therefore seems appropriate to determine what amount of irreversibility could account for the small, systematic deviations from Gor'kov's equations (3) and (8). This can be done by turning the argument around and analyzing our results on the supposition that these equations are, in fact, exact. Keeping $H_{c2}(t)$ unchanged, the theoretical values of $\kappa(t)$ then lead to

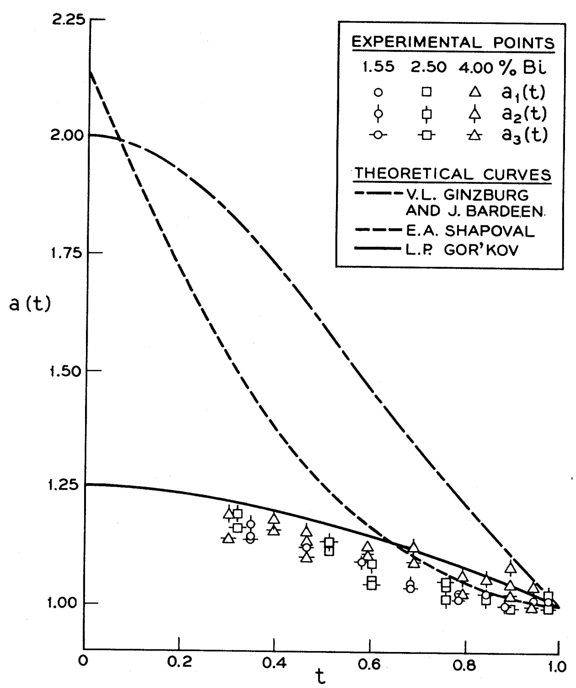

Fig. 2. Temperature dependence of $a(t) \equiv \kappa(t)/\kappa(1)$ for three typical samples, compared with different theoretical predictions. The subscripts 1, 2, and 3 refer to values deduced, respectively, from Eq. (6), from the ratio $H_{c2}(t)/H_{c1}(t)$, and from the slope of the magnetization curve near $H_{c2}(t)$.

values of $H_c(t)$ which are 4–9% lower than those calculated from the area under the magnetization curves. In other words, if irreversible effects resulted in magnetization curves with areas 8 to 18% larger than under reversible conditions, we could account for the fact that our values of $\kappa(t)$ are systematically low compared with Gor'kov's theory. Since we cannot rule out the possibility of such an irreversibility, we must conclude that the experimental results are probably consistent with Eq. (8).

THE CRITICAL VALUE OF $\kappa(t)$

The inference drawn from our results that the GLA theory can be applied at all temperatures implies that

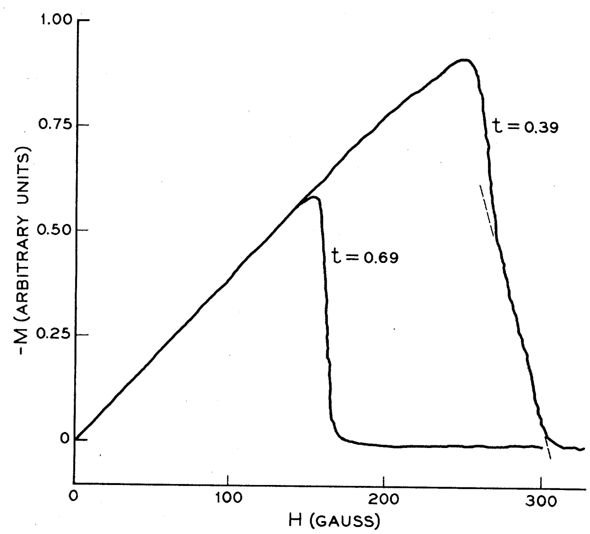

Fig. 3. The experimental magnetization curves in increasing magnetic field for the In–1.5 at. % Bi sample, taken from the magnetometer recordings for two temperatures.

the fundamental quantities continue at all temperatures to have the same physical significance which they have near the transition temperature. For any value of κ, H_{c2} is the absolute stability limit of the normal state in decreasing magnetic field.[1,14,15] The distinction between superconductors of the first and second kind lies in whether H_{c2} is smaller or larger than H_c. If smaller, there can be supercooling and the interphase surface energy must be positive: the superconductor is of the first kind. If $H_{c2} > H_c$, the superconductor is of the second kind. This of course means, according to Eq. (6), that at any temperature $\kappa = \frac{1}{2}\sqrt{2}$ is the critical value marking the change from one kind of superconductivity to the other. Thus, if near T_c a certain material is a superconductor of the first kind but with $0.57 \leqslant \kappa < 0.707$,[14] the gradual increase of $\kappa(t)$ with lowering temperature should bring about a change to second-kind behavior at that temperature at which $\kappa = \frac{1}{2}\sqrt{2}$. This supposition is confirmed by our results. In Fig. 3 we show the experimental magnetization curves at $t = 0.69$ and at $t = 0.39$ for the sample containing 1.50 at.% Bi. From the measured resistivity and Eq. (1) we find for this specimen $\kappa(1) = 0.62$. According to Eqs. (5) and (8) one would then have

$\kappa(0.69) = 0.69$ and $\kappa(0.39) = 0.75$, implying a change from first- to second-kind behavior between the two temperatures. Indeed, Fig. 3 shows a small but quite definite change in the shape of the magnetization curves, the one at $t = 0.39$ showing the break characteristic of the mixed state. Both the slope of this magnetization curve near H_{c2} and the ratio of H_{c2} to H_{c1} are consistent with a value of $\kappa = 0.75$.

That $\kappa = \frac{1}{2}\sqrt{2}$ remains the critical value at all temperatures is seen most clearly by comparing Figs. 4 and 5. On the former we plot as a function of

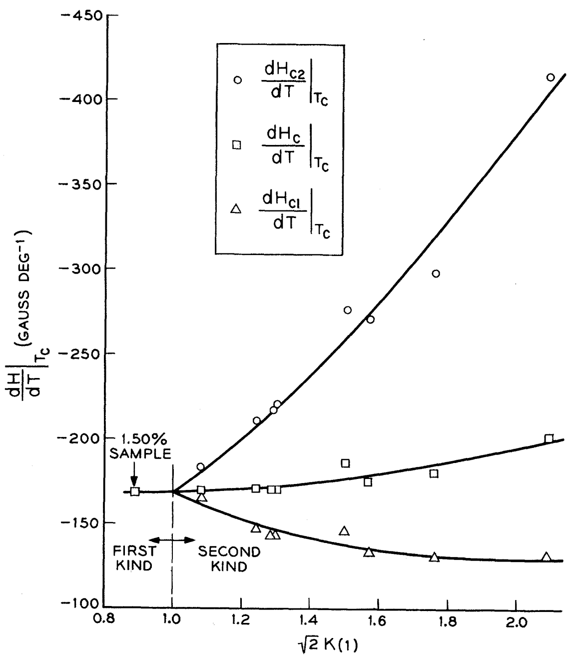

FIG. 4. The slopes of the three critical field curves at T_c of all the samples, plotted as a function of $\sqrt{2}\kappa(1)$. The 1.5 at. % sample has only a single critical field near T_c, and $\sqrt{2}\kappa(1)$ as calculated from Eq. (1) is less than unity.

$\sqrt{2}\,\kappa(1)$ the transition temperature limit of the slopes of the three critical fields. On the latter we plot the zero temperature limit of the critical fields themselves, this time as a function of $\sqrt{2}\,\kappa(0)$. In both figures, the curves converge at $\sqrt{2}\,\kappa = 1$, indicating that this marks the separation between first- and second-kind superconductors at 0°K as well as at T_c. The points for the 1.5% Bi specimen are to be noted. In Fig. 4 the value of $\sqrt{2}\,\kappa(1)$ as calculated from Eq. (1) is less than unity, whereas in Fig. 5 unity is exceeded by the value of $\sqrt{2}\,\kappa(0)$ which is calculated

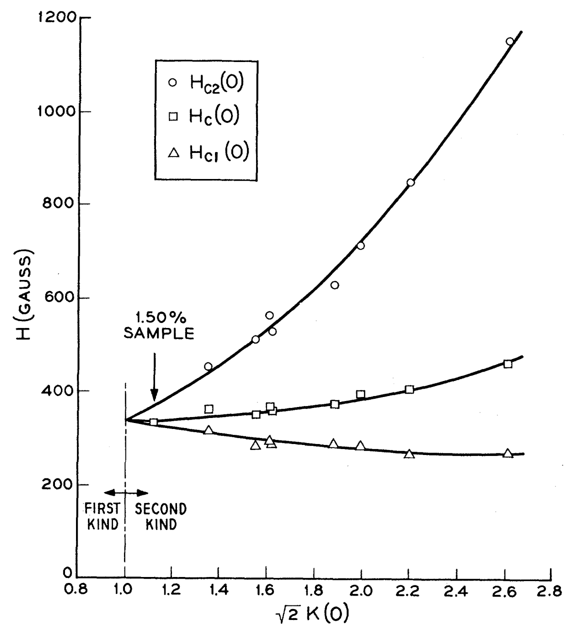

FIG. 5. The 0°K values of the three critical fields of all the samples, plotted as a function of $\sqrt{2}\kappa(0)$. For the 1.5 at. % sample unity is now exceeded by the value of $\sqrt{2}\kappa(0)$ as calculated from Eqs. (5) and (8) and consistent with the magnetization curve taken at $t = 0.39$.

from Eqs. (5) and (8) and is consistent with the experimental magnetization curves.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of A. Siemons and A. Demko in the design and construction of the apparatus, and the help given by L. Dubeck and G. Chang in performing the experiments. We are also grateful to Dr. Berlincourt and Dr. Hake for their kindness in sending us the results of their work before publication.

One of us (T. K.) wishes to thank the Socony-Mobil Company for financial assistance.