

Superconducting Transition in Zinc and Gallium*

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The superconducting transitions of Ga and Zn have been studied to compare the supercooling of these elements with that shown by Al under similar conditions. Both Ga and Zn show considerably less tendency to supercool than Al despite their lower critical temperatures. The measurements also provide values of T_c and $(dH_c/dT) T_c$ for Ga and Zn for comparison with recently reported calorimetric data. Attention is called to the fact that discrepancies still exist between direct calorimetric determination of the specific heat discontinuity at the critical temperature and the value deduced thermodynamically from critical field data. It is shown that such discrepancies are conspicuously worse among the elements Zn, Ga, and Al than for the elements of higher T_c (In, Sn, Ta, and Pb) where agreement is within experimental error.

INTRODUCTION

GENERAL arguments given by Pippard¹ predict that his range of coherence parameter ξ_0 should vary inversely with the critical temperature T_c of a superconducting element. Such a relationship is expected to lead to an increasing degree of supercooling in elements of decreasing T_c . General confirmation of this regularity is found in the circumstance that the elements of the sequence Pb ($T_c=7.18^\circ\text{K}$), Sn ($T_c=3.72^\circ\text{K}$), and Al ($T_c=1.19^\circ\text{K}$), show progressively larger amounts of supercooling. In the case of Al the tendency to supercool is strikingly pronounced.²⁻⁴

The present measurements on Ga and Zn (both of which have T_c values below that of Al) were undertaken to see whether these elements would show a degree of supercooling comparable with that of Al. The measurements also yield fairly reliable values for T_c of Ga and Zn which have not been frequently measured owing to the relative inaccessibility of their superconducting range.

EXPERIMENTAL

Measuring Technique

The present measurements were made using the same apparatus which has been described in two previous articles on the superconducting transition in Al.^{4,5} (For brevity these references will be designated as I and II hereafter.)

The Ga data were obtained using the apparatus of II which employs a paramagnetic salt pill for thermometry at the lowest temperatures. The apparatus of II proved incapable of reaching the critical temperature of Zn, and thus the apparatus of I was used with temperatures being determined from the critical field of a single

crystal of Al in thermal equilibrium with the Zn specimen.

Specimen Preparation

Zinc Specimens

Zinc single crystals were grown from 99.999% pure Zn (obtained from the New Jersey Zinc Sales Company). Specimens were prepared in 6-mm i.d. Pyrex tubing which was precoated with graphite, and using a gradient furnace similar to that described by Jillson.⁶ After crystallization, the Pyrex was cracked away from the specimens by thermal shocking at notches filed in the glass. Hydrofluoric acid could not be used to dissolve the glass because it attacked the Zn too rapidly. The resulting specimens were electroetched at the ends to remove strained material and to produce a hemispherical shape. Grain boundaries were revealed by etching in a 50% solution of HCl.

The above technique produced single crystals about half of the time. All such specimens were oriented with the C axis parallel to the cylinder axis, as determined by reflection of collimated light from etch pits. The single-crystal specimen used in the present measurements was 2.75 inches long and 0.22 inch in diameter.

Gallium Specimens

Gallium presents some unusual problems owing to: (a) its low melting point (29.7°C), (b) its tendency to supercool well below the melting point, and (c) the expansion which occurs in Ga upon solidification. Because of the expansion during crystallization, specimens were cast in tubes of the flexible and chemically inert plastic, Tygon, using the arrangement shown in Fig. 1. Tygon tubing of nominally 0.125-inch i.d. was stretched within a glass sleeve, the ends being held by the flared glass bushings. This scheme straightened the Tygon tubing and also reduced its bore slightly, thus facilitating subsequent removal of the gallium crystal when tension was released.

Crystals were cast from Ga of 99.95% purity supplied

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¹ A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

² D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940).

³ T. E. Faber, Proc. Roy. Soc. (London) **A231**, 353 (1955).

⁴ J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).

⁵ J. F. Cochran and D. E. Mapother, Phys. Rev. **111**, 132 (1958).

⁶ D. C. Jillson, Trans. Am. Inst. Mining Met. Engrs. **188**, 1005 (1950).

by the Aluminum Company of America. Molten Ga was sucked up to the required height in the mould through the lower glass bushing which was then sealed off. The ambient temperature of the room (in summer) provided a constant temperature bath of 28.5°C, slightly below the melting point. The supercooling of pure molten Ga is so pronounced that it will remain liquid for hours even when its temperature is reduced to 0°C. To initiate nucleation of the solid phase, the tip of the lower glass bushing was dipped into liquid nitrogen and subsequent crystallization was then allowed to proceed at 28.5°C. The solid-liquid interface moved through the mould at the rate of 2 to 4 cm per hour.

Upon completion of crystallization, the Tygon was cut away from the glass bushings at each end whereupon the Ga cylinders readily slipped out of the tubing. The whisker of metal at the bottom of the main cylindrical specimen was easily removed with a warm wire. To reveal grain boundaries, specimens were etched for three minutes in a chilled bath of aqua regia at 10°C. The Ga single crystals used in the superconductivity measurements were cylinders 2.125 inches long and 0.125 inch in diameter.

In order to prevent the specimens from melting while making the various solder joints necessary in loading the cryostat of II, the bottom ends of the specimen chambers were packed in dry ice.

RESULTS

Measurements on Zinc

The lowest stable temperature which could be reached was about 0.03°K below T_c for Zn. Since conditions were so unfavorable, only one specimen was measured and at only two different temperatures. The observed transitions are shown in Fig. 2 where the effective permeability, μ_e , is plotted vs the applied field. The behavior at the lowest temperature [Fig. 2(b)] showed all the qualitative properties previously seen in superconducting transitions of Al including supercooling and the quench effect. The S - N (superconducting-normal) transition widths are broad, showing apparent demagnetizing factors of 0.36 and 0.13 in comparison with the value, $n=0.01$, expected on the basis of specimen geometry.⁷ Similar broadening in the transition occurs in Al near its critical temperature.

It is questionable whether any supercooling occurs in the transition shown in Fig. 2(a), although the transition in decreasing field is clearly displaced below that in increasing field. Because of the small H_c value at this temperature, the step width in the experimental variation of H_c (limited by considerations of galvanometer sensitivity⁴) is too great to give good resolution of the discontinuous drop in μ_e expected for a supercooled transition. The value of $H_s(\text{Zn})$ at this temperature is taken to give the largest degree of supercooling consistent with the observed data.

⁷ E. C. Stoner, Phil. Mag. 36, 803 (1945).

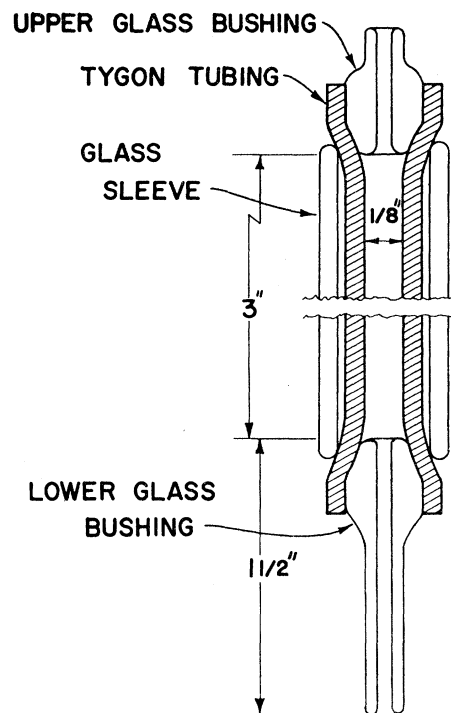


FIG. 1. Flexible mould for casting gallium single crystals.

The data obtained in these measurements were as follows:

	$H_c(\text{Zn})$	$H_c(\text{Al})$	$H_s(\text{Zn})$	T (°K)
Obs. 1	0.91	47.4	0.81(?)	0.864
Obs. 2	2.32	49.6	2.05	0.846

$H_c(\text{Zn})$ and $H_c(\text{Al})$ denote critical fields (in gauss) of the indicated elements observed under conditions of mutual thermal equilibrium, $H_s(\text{Zn})$ is the value of the observed supercooled transition in Zn, and temperature values are deduced from $H_c(\text{Al})$ using the results of II.

Extrapolation of the two critical field points to zero field gives a critical temperature of Zn of $0.875 \pm 0.01^\circ\text{K}$. The limiting value of the slope of the critical field curve gives $(dH_c/dT)_{T_c} = -83.5 \pm 2.5$ gauss/deg, and, as discussed below, this is a considerably smaller value than might be expected.

Measurements on Gallium

A relatively wider range of temperature was available in observations on Ga and data were obtained for two specimens (called Ga-1 and Ga-2). Typical S - N transitions are shown in Fig. 3, where the critical field values of Ga-1 and Ga-2 agree within about 0.5%. The widths of the transitions are in excellent agreement with the value expected on the basis of specimen geometry over the entire temperature range of observation, a result in striking contrast with the behavior of Al and Zn near their critical temperatures. Near T_c the Ga transition

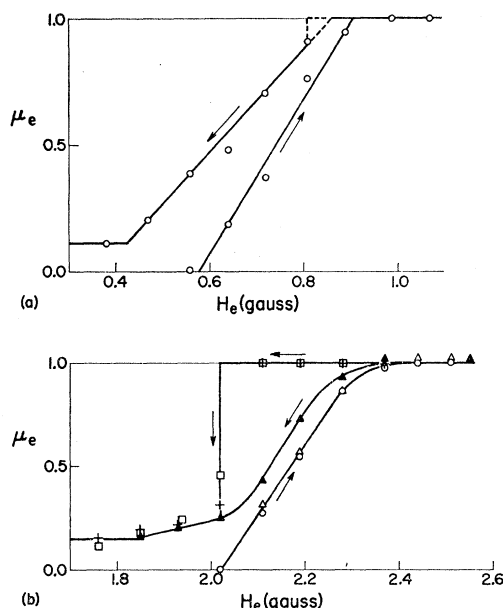


FIG. 2. Superconducting transitions in Zn specimen. (a) $H_c(\text{Al}) = 47.4$ gauss, $T = 0.864^\circ\text{K}$. The N - S transition, although displaced to lower fields than the S - N transition, does not show clear evidence of supercooling. (b) $H_c(\text{Al}) = 49.6$ gauss, $T = 0.846^\circ\text{K}$. Definite supercooling occurs when H_c is increased sufficiently above H_c . Three observations are shown: 1. $H_c(\text{max}) \sim 2.6$ gauss, Δ (H_c increasing), \blacktriangle (H_c decreasing). 2. $H_c(\text{max}) = 10$ gauss, \circ (H_c increasing), $+$ (H_c decreasing). 3. $H_c(\text{max}) = 50$ gauss, \square (H_c decreasing).

occurred within a field interval of 0.08 gauss, or, taking into account the value of $(dH_c/dT)_{T_c}$ for Ga, equivalent to a temperature interval of about $\frac{3}{4}$ millidegree. This observation suggests that the surface free energy for Ga is relatively small (see Appendix II).

The transitions were reversible (providing the applied field did not exceed H_c), showed a fairly large supercooling effect, and specimen 1 exhibited a quench effect⁴ (see Fig. 4). No attempt was made to record the quench field H_q since it was very erratic, showing widely scattered values during successive observations at a single temperature.

The critical field of Ga is plotted as a function of T^2 in Fig. 4 together with data for the supercooled transitions. The H_c values for the two specimens agreed within 0.1 gauss over the range of observations and so these points are not distinguished in Fig. 4. The curve of H_c vs T^2 was linear to within the experimental error, and was fitted by least squares to a straight line with the following results:

$$H_c(T) = (54.3 \pm 0.3) - (45.6 \pm 0.3)T^2.$$

From this expression we obtain the value, $T_c = 1.091 \pm 0.005^\circ\text{K}$, where the probable errors include a contribution due to the uncertainty in the salt pill calibration. The limiting slope of the critical field curve gives $(dH_c/dT)_{T_c} = (99.5 \pm 1.0)$ gauss/deg.

DISCUSSION

Supercooling Behavior

The supercooling behavior of a specimen may be characterized by plotting the field of the supercooled transition H_s against the critical field H_c of the specimen at the same temperature.⁸ Such a plot is given in Fig. 5 and contains points near T_c for Ga-2 (which showed the greatest supercooling of the Ga specimens) and the 2 points for Zn. The curve marked Al gives some typical results in corresponding measurements on specimen 19 of II, while the light line inclined at 45° corresponds to the case of no supercooling.

The Zn data are admittedly fragmentary although the two observations shown were made very near T_c , which is the most significant region for determining the supercooling properties. It is clear from Fig. 5 that the supercooling tendency observed here is just the reverse of that expected on the basis of Pippard's arguments. However, the conclusion is not so obvious as these results seem to suggest.

It should be noted that the present measurements give the average supercooling behavior of the entire specimen. The extensive work of Faber^{8,9} has shown that the intrinsic supercooling of superconducting elements (to which Pippard's predictions apply) is, in some cases, very sensitive to the presence of "flaws" in the specimen under observation. The nature of such "flaws" is not entirely clear, but considerable evidence suggests that they occur in microscopic regions of strain within the crystal lattice. Both Ga and Zn possess anisotropic thermal expansion coefficients. This fact can be expected to militate against efforts to prepare suitable "flaw-free" specimens, even when, as in the present case, the specimens are carefully prepared single crystals.

We think it safe to conclude that bulk specimens of

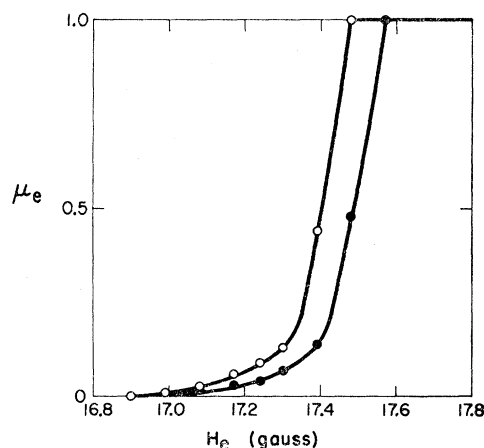


FIG. 3. Typical S - N transitions of two gallium specimens at $T \sim 0.90^\circ\text{K}$ (\circ , Ga-1; \bullet , Ga-2). Supercooled transitions occur for both specimens at fields which are far off the scale of this figure (see Fig. 4).

⁸ T. E. Faber, Proc. Roy. Soc. (London) **A241**, 531 (1957).

⁹ T. E. Faber, Proc. Roy. Soc. (London) **A214**, 392 (1952).

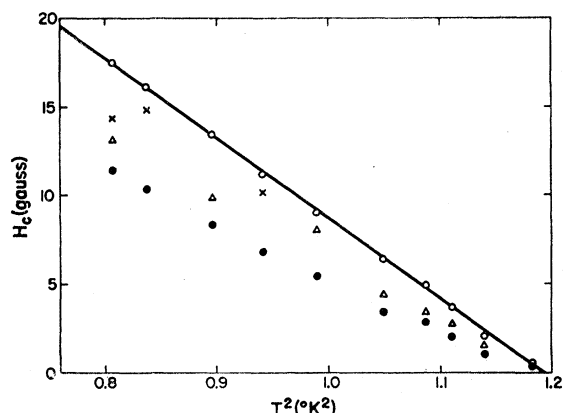


FIG. 4. Critical field curve and supercooling results for two gallium specimens. Critical field values for both specimens are indistinguishable on this scale and are shown by \circ . Supercooled transitions are identified as follows: \circ —unquenched, \triangle —quenched; Ga-2; \bullet (no quench effect observed).

Ga and Zn fail to show the strong tendency to supercool which is so easily observed with Al. However, it is not possible on the basis of the present work to separate the relative importance of lattice defects from intrinsic surface energy effects at the superconducting phase boundary.

Critical Field Curve Parameters

Observed values of the critical temperature and the slope of the critical field curve at T_c are listed in Table I together with values for the specific heat discontinuity, ΔC . The value of ΔC at T_c may be computed from critical field data using Rutgers' equation¹⁰

$$\Delta C = \frac{V_m T_c}{4\pi} \left(\frac{dH_c}{dT} \right)_{T_c}^2,$$

where V_m is the molar volume. Values so calculated are followed by the note (mag). The specific heat discontinuity is also directly observable in calorimetric measurements and recently reported values are listed for comparison, followed by the note (cal). Corresponding data for Al are also included in Table I for comparison.

With but few exceptions, agreement between the various measurements of T_c is acceptably good even though in many instances the small differences exceed the stated experimental error. The worst disagreement in T_c occurs in the case of Zn where values spread over a temperature range of about $0.1T_c$. Unless Zn proves itself exceptional among the soft elemental superconductors in showing a pronounced dependence of T_c upon the mode of specimen preparation, these differences must be attributed to the vagaries of absolute temperature determinations below 1°K .

Concerning values of $(dH_c/dT)_{T_c}$, the present low value for Zn is noteworthy, since, despite the poor

TABLE I. Comparison of magnetic and calorimetrically determined critical field constants for Zn, Ga, and Al.

Element	T_c ($^\circ\text{K}$)	$(dH_c/dT)_{T_c}$ (gauss/deg)	ΔC (millijoules/ mole deg)	Source
Zinc ($V_m = 9.03$ cc) ^a	0.875	-83.5	0.43 (mag)	This work
	0.905	-116	...	Goodman and Mendoza ^b
	0.861 ^c	...	0.61 (cal)	Seidel and Keesom ^d
	0.825	...	0.68 (cal)	Phillips ^e
Gallium ($V_m = 11.8$ cc) ^f	1.091	-99.5	1.02 (mag)	This work
	1.103	-91.2	...	Goodman and Mendoza ^b
	1.097 ^g	...	0.93 (cal)	Seidel and Keesom ^d
	1.085	...	0.96 (cal)	Phillips ^e
Aluminum ($V_m = 9.87$ cc) ^h	1.196	-165.2	2.57 (mag)	Cochran and Mapother ^b
	1.197	-177	...	Goodman and Mendoza ^b
	1.172	-164	2.46 (mag)	Faber ⁱ
	1.162	...	2.06 (cal)	Phillips ^k
	1.178	(microwave measurements)	...	Biondi and Garfunkel ^l

^a Corrected for thermal contraction using results of H. L. Laquer, Atomic Energy Commission Report AEC-D-3706 (Office of Technical Services, Department of Commerce, Washington, D. C.).

^b See reference 11.

^c Corrected for effect of earth's magnetic field.

^d See reference 12.

^e See reference 15.

^f Value characteristic of 20°C . No thermal expansion data at low temperatures are available for Ga.

^g N. E. Phillips (private communication).

^h See reference 5.

ⁱ Corrected for thermal contraction using results of B. F. Figgins, G. O. Jones, and D. P. Riley, Phil. Mag. 1, 747 (1956).

^j See reference 3.

^k See reference 16.

^l M. A. Biondi and M. P. Garfunkel, Phys. Rev. 116, 853 (1959).

circumstances of measurement, the value reported here is probably accurate to about $\pm 5\%$. About half the difference between our value and that of Goodman and Mendoza¹¹ is due to the nonparabolic shape of the critical field curve of Zn¹² which was not known at the time of the earlier measurements. The remaining difference appears to suggest that Zn shows the same decrease in the magnitude of (dH_c/dT) near T_c that was previously

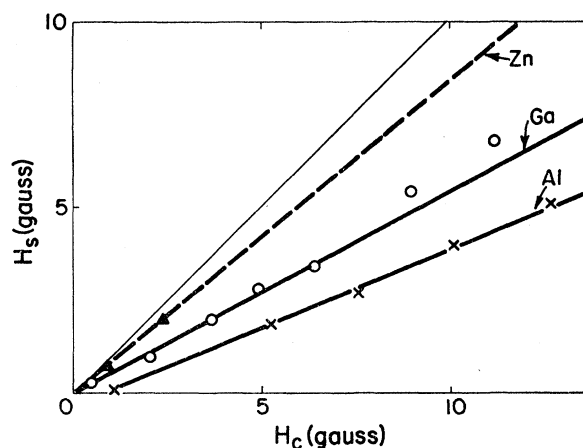


FIG. 5. Comparative supercooling tendencies shown by zinc, gallium, and aluminum under similar experimental conditions. Light line inclined at 45° corresponds to no supercooling; decreasing slope corresponds to increasing supercooling effect.

¹⁰ D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), Chap. III.

¹¹ B. B. Goodman and E. Mendoza, Phil. Mag. 42, 594 (1951).

¹² G. Seidel and P. H. Keesom, Phys. Rev. 112, 1083 (1958).

reported for Al.⁵ The abnormal width of the magnetic transitions in Zn is also similar to the effect noted in Al.

Agreement between the magnetic and calorimetric determinations of ΔC is not as good as it ought to be in view of the estimated experimental uncertainty. The case of Zn shows such great discrepancy that it seems advisable to defer any attempt at explanation until further data are available.

Disagreement in ΔC values is not great in the case of Ga although it is somewhat outside the experimental error (about 1–2% for the calorimetric data and possibly as much as 3% for the magnetic data). A major uncertainty in $\Delta C(\text{mag})$ results from the present lack of information concerning the thermal expansion of Ga.¹³

The case of Al presents the worst disagreement. Despite evident variation in reported T_c values, the critical field measurements seem self-consistent within a few percent. The calorimetric data appear to be of excellent quality and should yield $\Delta C(\text{cal})$ with a precision of 1–2% at worst. However, $\Delta C(\text{mag})$ exceeds $\Delta C(\text{cal})$ by about 20%.

It is of interest to compare the agreement between $\Delta C(\text{mag})$ and $\Delta C(\text{cal})$ for some elements of higher T_c for which complete data are available. Results for four elements are given in Table II, and it is evident that agreement is excellent except for the case of Pb.¹⁴ The general conclusion from the data of Table II is that Rutger's equation is very well confirmed. It is, therefore, strange that measurements of apparently equal quality produce such discrepancies as are displayed in Table I.

It seems probable that the disagreement in the case of Al arises from inaccuracy in $(dH_c/dT)T_c$. The H_c measurements on Al⁵ showed a reduction in slope near T_c which was disregarded in calculating the results. Reanalysis of the earlier data considering only points for which $T^2 > 1.22$, yields a value of $(dH_c/dT)T_c$ which is in much better agreement with the calorimetric result. However, owing to the difficulties in fixing H_c described earlier,⁵ there is considerable scatter. New measure-

TABLE II. Verification of Rutgers' equation for In, Sn, Ta, and Pb.^a

	T_c (°K)	V_m (cm ³)	$(dH_c/dT)T_c$ (gauss/deg)	$\Delta C(\text{mag})$ (millijoules/ mole deg)	$\Delta C(\text{cal})$ (millijoules/ mole deg)
In	3.408	15.33 ^b	–152	9.62 ^c	9.75 ^b
Sn	3.722	16.1	–148.8	10.56 ^c	10.6 ^d
Ta	4.482	10.9	–327	41.6 ^e	41.5 ^e
Pb	7.175	17.85 ^f	–238.4	58.1 ^f	53.0 ^g

^a The $\Delta C(\text{cal})$ values for both In and Pb were measured using the "1948 Scale" of temperature. However, the correction to the 1958 He⁴ Scale is negligible in the case of In, and the Pb results were not reported in sufficient detail to permit a correction. Except for Pb, all $\Delta C(\text{cal})$ values were re-evaluated from the original data.

^b J. R. Clement and E. H. Quinell, Phys. Rev. **92**, 258 (1953).

^c R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

^d W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

^e D. White, C. Chou, and H. L. Johnston, Phys. Rev. **109**, 797 (1958).

^f D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).

^g J. R. Clement and E. H. Quinell, Phys. Rev. **85**, 502 (1952).

ments of H_c for Zn, Ga, and Al near T_c would be desirable to clarify this point and also to fix the T_c values with greater precision.

In Table I we have not included the ΔC values computed from the work of Goodman and Mendoza. Their $(dH_c/dT)T_c$ values, based on an assumed parabolic critical field curve, are strongly biased by data observed well below T_c . Recent calorimetric measurements^{12,15,16} imply nonparabolic critical field curves for all of these elements with deviations of such magnitude as to require an approximately 15% reduction in the originally quoted values of $(dH_c/dT)T_c$. This leads to modifications in the value of ΔC of about 30%, which is larger than the magnitude of the discrepancies between $\Delta C(\text{mag})$ and $\Delta C(\text{cal})$ that are under consideration. It was felt that significant corrections of this magnitude could not be applied to the older data. The values of T_c in the earlier work are not seriously affected by these considerations and appear to be of accuracy comparable to that of the present work.

ACKNOWLEDGMENTS

We are grateful to R. S. Kaeser for his valuable contributions in the preparation of the single-crystal specimens and for his assistance with the measurements. Our thanks go to N. E. Phillips for making his results on Ga available to us in advance of publication.

¹⁵ N. E. Phillips, Phys. Rev. Letters **1**, 363 (1958).

¹⁶ N. E. Phillips, Phys. Rev. **114**, 676 (1959).

¹³ A volumetric change of 6% due to thermal contraction between 20°C and 1°K would be necessary to produce agreement with the nearest value of $\Delta C(\text{cal})$ for the case of Ga if this was the sole cause of the difference. This seems unreasonably large.

¹⁴ Observation of $\Delta C(\text{cal})$ is difficult since $\Delta C/C_n \approx 0.05$ for Pb (where C_n is the normal specific heat at T_c). Thus an accuracy of 1% in $\Delta C(\text{cal})$ for Pb would require measurements of C_n and C_c accurate to 0.05%. This is very difficult to achieve in low-temperature calorimetric measurements. A much more favorable situation exists in the case of Zn, Ga, or Al (where the ratios, $\Delta C/C_n$, are, respectively, 0.97, 1.27, and 1.27) and the accuracy of ΔC should be about the same as that obtained in the value of C_n .