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Isotope effect in superconducting β-phase gallium

Hugo Parr*
Fysisk Institutt, Universitetet i Oslo, Oslo 3, Norway
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The superconductive isotope effect in β-phase Ga has been investigated in small single spheres of ^{69}Ga and ^{71}Ga. The difference in transition temperatures is $\Delta T_c = 73 \pm 3$ mK. Assuming a dependence on the mean isotopic mass of the form $T_c \sim M^{-\alpha}$, this yields $\alpha = 0.43 \pm 0.02$. The transition temperatures are $T_c^{69} = 6.10 \pm 0.02$ K and $T_c^{71} = 6.02 \pm 0.02$ K. Our previously published value for T_c in β-Ga is too low owing to an incorrect thermometer calibration. The correct value is $T_c^{\beta} = 6.07 \pm 0.03$ K for natural β-Ga. $H_c(T)$ has been measured both for ^{69}Ga and ^{71}Ga. At $T = 0$, the difference in critical field is $H_0^{69} - H_0^{71} = 5 \pm 2$ Oe, in agreement with the similarity principle. Within the experimental accuracy, the deviation of $H_c(T)$ from a parabola is independent of isotopic mass, yielding $D(t^2)_{max} = -0.021 \pm 0.004$. The slope $(dH_c/dT)|_{T_c} = 155 \pm 2$ Oe/K, independent of isotopic mass to this accuracy. These results show β-Ga to be a rather typical weak-coupling superconductor.

INTRODUCTION

The study of small single spheres of superconducting materials using a mutual induction method has proved to be an excellent tool for investigating superheating and supercooling at the superconductive phase transition.[1,2] The success of this method rests on the production of nearly flawless small spheres, permitting the study of metastable states unobservable in a bulk sample because of inhomogeneous nucleation caused by defects. However, as shown in our previous work on β-phase Ga,[2] the technique can also be useful in studying the critical-field curve and the intermediate state. In this case, less-than-perfect spheres are deliberately selected, because the large degree of superheating would prevent any perfect sphere from ever entering into the intermediate state.[2]

Since β-phase Ga is metastable at atmospheric pressure, and is thus not readily obtained in large bulk samples, the single-sphere method is very well suited to the study of its superconductive properties. In the following, we report measurements of the transition temperature T_c and the critical-field curve $H_c(T)$ for β-phase ^{69}Ga and ^{71}Ga. These experiments were partly motivated by our earlier results on $H_c(T)$ in β-Ga, as published in Fig. 5 of Ref. 2. These results indicated an anomalous deviation from a parabolic temperature dependence, resembling the strong-coupling superconductors Hg and Pb. As explained in the following, the anomaly arose because of an incorrect thermometer calibration. In fact, β-Ga will be shown to be a rather typical weak-coupling superconductor.

EXPERIMENTAL

The sample preparation has been described earlier.[2] The isotopes, ^{69}Ga and ^{71}Ga, were obtained from Oak Ridge National Laboratory.[4] Both isotopes are chemically pure to 99.9%. Spectrographic analysis shows impurities to be present at approximately the same levels in both isotopes. In particular, Fe is present in both isotopes at the 200-ppm level. Thus impurities should not influence the measured difference in superconductive transition temperatures.

In our previous experiments[2] on nearly perfect natural Ga spheres, ranging in diameter from 7 to 26 μm, all spheres turned out to be in the β phase. In the present experiments, less-than-perfect spheres of diameters between 20 and 30 μm were selected. Of the six ^{71}Ga spheres investigated, five were in the β phase, whereas only three out of eight ^{69}Ga spheres were in the β phase. The remaining spheres presumably crystallized in the α phase since no superconductivity was seen above 2 K, and since these spheres turned out to be solid at 20 °C after being warmed up from low temperatures. Thus, the β phase may be more strongly metastable in ^{69}Ga than in natural Ga or ^{71}Ga. In a total of 25 Ga spheres investigated in our present and past single-sphere experiments, we have found no evidence for the metastable δ, γ, and ε phases, all reported to be superconducting above 4.2 K.[3]

The cryostat and detection system used are the same as in our previous experiments.[2] However, we have found an error in the calibration of our germanium thermometer for temperatures above 4.2 K. The error has been traced to our original calibration of this thermometer against a factory calibrated Ge thermometer. It arose because of differences in electrical lead dimensions and lead insulation, causing a difference in thermal anchoring for the two thermometers. As a consequence, the transition temperature reported for β-Ga, 5.90 K, is too low. A thorough recalibration

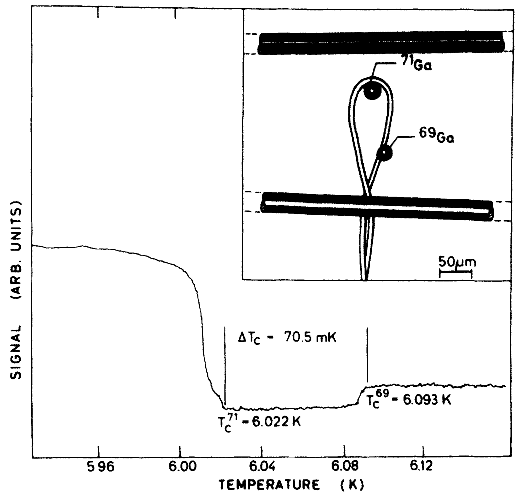

FIG. 1. Upper right: sample holder for the isotope-effect experiment, drawn from a photograph. Leads are glued with varnish to a polished copper surface. Spheres shown have diameters of 26 μm (sample 71-4) and 23 μm (sample 69-4). Lower left: actual recorder trace of the zero-field superconducting transitions of these spheres. This measurement gives not only the magnitude of the isotope effect, but also its sign, the larger signal obviously belongs to the 71 sphere *inside* the pickup loop.

shows it to be

$$T_c^\beta = 6.07 \pm 0.03 \text{ K} .$$

Because of this calibration error, the reported temperature dependence of $H_c(T)$ (Fig. 5 of Ref. 2) is also incorrect. The corrected results are presented below. No other results from our previous work on β-Ga are affected. In particular, the reported results on the Ginzburg-Landau parameter κ and the penetration depth δ (T) remain unchanged.

After the recalibration of our germanium thermometer, the absolute error in our temperature readings are less than 8 mK below 4.2 K and less than 20 mK in the region 4.2–7 K. The temperatures are traceable through secondary standards to the NBS-65 provisional scale.

RESULTS

We present below the results of measurements of T_c and $H_c(T)$ carried out on three ^{69}Ga and five ^{71}Ga spheres, of diameters ranging between 20 and 30 μm.

Fig. 1 shows how the isotope effect can be determined directly by a temperature sweep in zero field. The sample holder contains two spheres, one of each isotope. One sphere is placed inside the pickup loop, the other on the outside. Therefore, the two transition signals will be approximately 180° out of phase. This makes it easy to distinguish the two signals, as is seen from the figure. By this direct measurement of the difference in transition temperatures, most systematic errors are eliminated. In particular, the small dimensions involved rule out any field or temperature gradients. Measurements of this type yield

$$\Delta T_c = 73 \pm 3 \text{ mK} .$$

Assuming as usual that the transition temperature depends on the isotopic mass M as $T_c \sim M^{-\alpha} = M^{-0.5(1-\zeta)}$, substitution of the isotopic masses yields

$$\alpha = 0.43 \pm 0.02 , \quad \zeta = 0.15 \pm 0.04 .$$

In Fig. 1, the filling factor is fair for the 71 sphere, and poor for the 69 sphere lying outside the pickup loop. Figure 2 shows the superconductive transition for a 71 sphere with an improved filling factor. Figures 1 and 2 illustrate the resolution of the single-sphere method. In absolute terms, the transition temperature for the 71 and 69 isotopes are found to be 6.024 and 6.097 K, respectively. The thermometer calibration introduces a 20-mK uncertainty. We thus obtain

$$T_c^{71} = 6.02 \pm 0.02 \text{ K} , \quad T_c^{69} = 6.10 \pm 0.02 \text{ K} .$$

The transition temperature of natural β-Ga is (corrected from the earlier experiments)

$$T_c^\beta = 6.07 \pm 0.03 \text{ K} .$$

Figs. 3(a) and 3(b) give the results of measurements of $H_c(T)$ for the two isotopes. $H_c(T)$ is determined by sweeping the magnetic field through the intermediate state to progressively higher values, until supercooling occurs upon reduction of the field. (Explained in detail in Sec IV B and

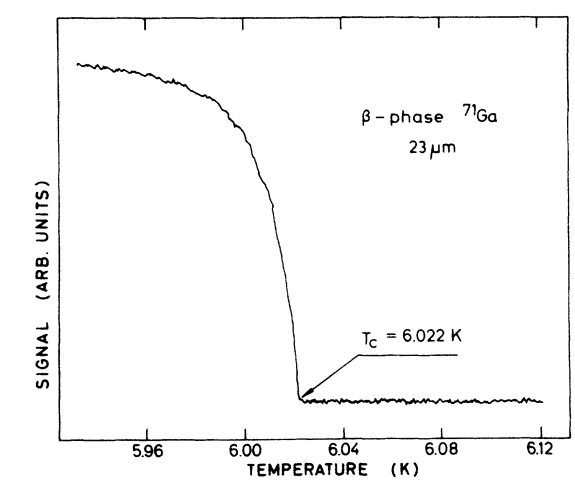

FIG. 2. Recorder trace showing the zero-field superconducting transition of sphere 71-7, of diameter 23 μm. This sphere has a better filling factor than those shown in Fig. 1. The accompanying ^{69}Ga sphere crystallized in the α-phase, therefore yielding no transition.

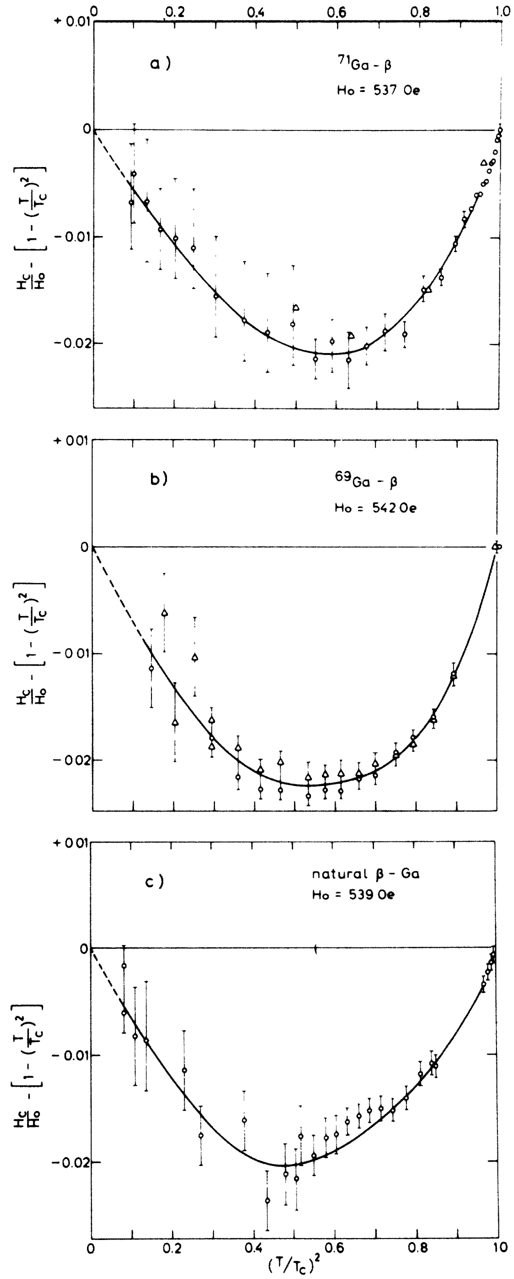

FIG. 3. Deviation of $H_c(T)$ from a parabolic temperature dependence for β-Ga. Solid curves are fitted by eye. (a) Data for ^{71}Ga. Circles: sphere 71-7 (T_c = 6.0221 K, diameter 23 μm). Triangles: sphere 71-6 (T_c = 6.0035 K, diameter 21 μm). (b) Data for ^{69}Ga. Circles: sphere 69-1 A (T_c = 6.1005 K, diameter 23 μm). Triangles: sphere 69-1 B (T_c = 6.0970 K, diameter 23 μm). (c) Data for natural Ga sphere of diameter 26 μm. The data in (c) were originally presented in Fig. 5 of Ref. 2 using an incorrect temperature scale above 4.2 K .

Fig. 4 of Ref. 2). The results are presented in the customary way, as a deviation from a parabolic temperature dependence. H_0 is determined by extrapolation for each isotope. T_c is determined individually for each sphere from a zero-field temperature sweep, like that in Fig. 2.

In Fig. 3(c), we have re-analyzed the data on $H_c(T)$ in natural β-Ga which we originally published using the erroneous temperature scale. The results are now quite unambiguous. The measurements close to T_c are consistent with the measurements at lower temperatures, and there is no sign of a size effect in H_c near T_c, as originally suggested. Indeed, no size effect would be expected in a 20-μm sphere on theoretical grounds, and the measurements on ^{69}Ga and ^{71}Ga give no indications of any size effect. Also, the field H_1 reported in Fig. 7 of Ref. 2 has not been reproduced in the present series of experiments, although similar intermediate-state curves have been observed. The entry and expulsion of flux in the intermediate state varies from one sphere to the next in a seemingly random way.

Within experimental accuracy, the three deviation curves of Fig. 3 are seen to be approximately the same. No systematic dependence on isotopic mass is discernible with the present resolution. Figure 4 gives the best fit of the deviation curve $D(t^2)$, characteristic of β-Ga. It is a weighted arithmetic sum of the curves in Fig. 3 and thereby takes account of all measurements that have been made. We conclude that for β-Ga

$$D(t^2)_{max} = -0.021 \pm 0.004 .$$

The uncertainty is mainly due to the ± 20-mK accuracy of the thermometer near T_c.

The isotope effect manifests itself not only in a difference in transition temperatures, but also,

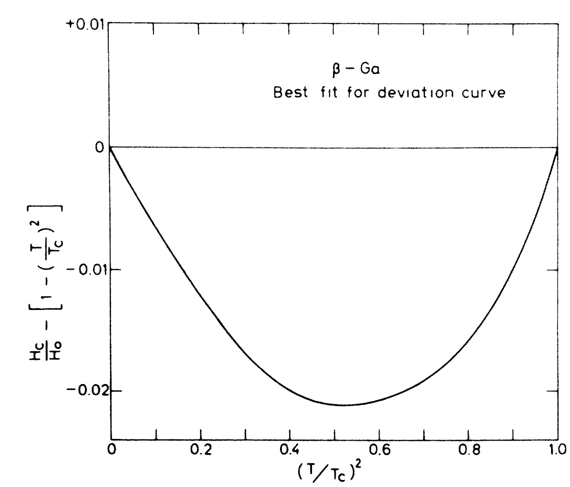

FIG. 4. Deviation of $H_c(T)$ from a parabola, best fit characteristic of β-phase Ga. This curve was obtained by adding the three curves in Fig. 3(a), (b), and (c), weighted by the ratios 0.8 : 1.2 : 1. It thus takes account of all measurements performed.

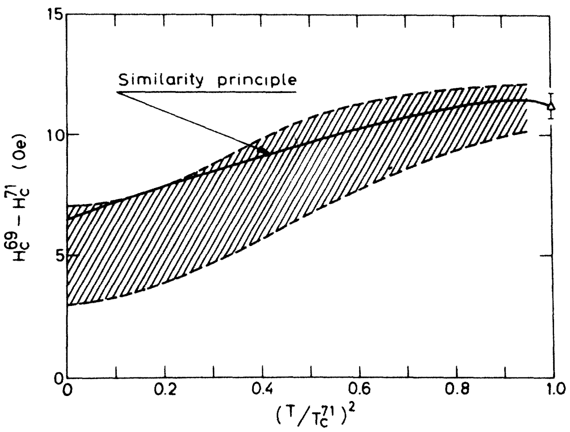

FIG. 5. Hatched area indicates difference in critical fields, $\Delta H_c = H_c^{69} - H_c^{71}$, as a function of temperature. This difference was obtained by subtracting the curves in Figs. 3(b) and 3(a). Triangle at T_c indicates measurement of isotope effect in zero field, as in Fig. 1. Full curve gives predicted $\Delta H_c(T)$ from the measured ΔT_c and the principle of similarity (see text).

of course, in a difference $\Delta H_c(T)$ in critical magnetic field. This difference is usually discussed in terms of the "similarity principle".[5,6] This principle requires that the ratio H_0/T_c be a constant independent of isotopic mass, and that the critical-field curves be identical when expressed in reduced coordinates; i.e., $D(t^2)$ must be the same for all isotopes. In Fig. 5, we have plotted $\Delta H_c(T) = H_c^{69}(T) - H_c^{71}(T)$ as predicted from ΔT_c and the similarity principle. The shaded area indicates the experimental values of ΔH_c, obtained by subtracting the curves of Figs. 3(b) and 3(a). The similarity principle is seen to be verified within the experimental accuracy. In particular, at $T = 0$

$$\Delta H_0 = 5 \pm 2 \text{ Oe} ,$$

in fair agreement with the similarity principle, which predicts $\Delta H_0 = 6.5$ Oe. In absolute terms, we find

$$H_0^{71} = 537 \pm 5 \text{ Oe} , \quad H_0^{69} = 542 \pm 5 \text{ Oe} .$$

The error reflects the 1% accuracy of the magnet calibration. The best value of H_0 for natural β-Ga, on the basis of all measurements which have been performed, is

$$H_0^{\beta} = 540 \pm 5 \text{ Oe} .$$

Finally, Fig. 6 shows the measurements of $H_c(T)$ very close to T_c, for natural Ga (earlier experiments) and ^{71}Ga. A least-squares fit to the data shown gives $dH_c/dT|_{T_c} = 153.7 \pm 1$ Oe/K for ^{71}Ga and 155.7 ± 2 Oe/K for natural Ga. Thus, within experimental accuracy, the slope is independent of isotopic mass. We conclude that for β-Ga

$$\left.\frac{dH_c}{dT}\right|_{T_c} = 155 \pm 2 \frac{\text{Oe}}{\text{K}}$$

DISCUSSION

Our value for the isotope-effect coefficient in β-Ga, $\alpha = 0.43 \pm 0.02$, is rather close to that found for α-Ga, 0.41 ± 0.02.[7] They both deviate significantly from the BCS value of 0.5.

Knowing α and T_c for β-Ga, we can compute the coupling parameters λ and μ^* which enter into McMillan's theory of superconductivity.[8] However, this requires an estimate of the Debye temperature. No value of Θ_D has been published for β-Ga, but an estimate can be made from the specific-heat measurements of Bosio *et al.*[9] They measured the specific heat of β-Ga relative to that of α-Ga from 150 K to the melting point of β-Ga, 257 K. Assuming that the lattice contribution to the specific heat dominates in both phases and that the specific heat scales simply with Θ_D, examination of their results (Fig. 3 of Ref. 9) shows that Θ_D of β-Ga must be about 70% of that of α-Ga, i.e.:

$$\Theta_D^{\beta} \approx 0.7 \times 325 \text{ K} \approx 228 \text{ K} .$$

Substituting α, T_c, and Θ_D into McMillan's equations (Eqs. 25 and 30 of Ref. 8, the approximation Eq. 29 has not been used), we find that for β-Ga

$$\lambda = 0.75 , \quad \mu^* = 0.13 .$$

Another coupling parameter of interest is $N(0)V$,

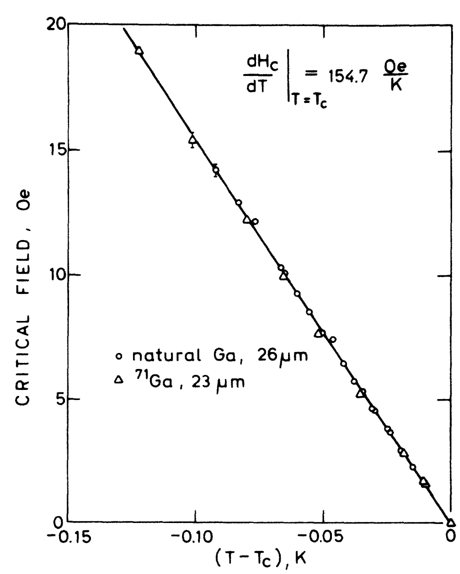

FIG. 6. Measurements of $H_c(T)$ close to T_c. Circles: natural Ga, sphere diameter 26 μm. Triangles: ^{71}Ga, sphere diameter 23 μm (sample 71-7, these data are also shown in Fig. 3).

TABLE I. Thermodynamic properties of superconducting β-Ga.

Quantity	Symbol	Value	Unit
Transition temperature	T_c	6.07 ± 0.03	K
Critical field at $T=0$	H_0	540 ± 5	Oe
Slope of $H_c(T)$ at T_c	$\left.\frac{dH_c}{dT}\right\|_{T_c}$	-155 ± 2	Oe/K
Curvature of $H_c(T)$ at $T=0$	$\left.\frac{d^2H_c}{dT^2}\right\|_0$	-31.2 ± 0.5	$(\mathrm{Oe/K})^2$
Maximum deviation of H_c from a parabola	$D(t^2)_{max}$	-0.021 ± 0.04	...
Isotope-effect coefficient	α	0.43 ± 0.02	...
Electronic-specific-heat coefficient	$\gamma = -\frac{1}{4\pi} H_0 \left.\frac{d^2H_c}{dT^2}\right\|_0$	1340 ± 20	$\mathrm{erg/K^2\ cm^3}$

occurring in BCS theory,[10]

$$N(0)V_{expt} \cong [\ln(0.85\,\Theta_D/T_c)]^{-1} \cong 0.29 \ .$$

These values of the coupling parameters show that β-Ga is definitely not a strong-coupling superconductor. Rather, it resembles materials like Sn [$\lambda = 0.60$, $N(0)V = 0.25$], In [$\lambda = 0.69$, $N(0)V = 0.29$], and Tl [$\lambda = 0.71$, $N(0)V = 0.27$].[8,10]

Indeed, the deviation of $H_c(T)$ from a parabolic temperature dependence, Fig. 4, shows β-Ga to be a weak-coupling superconductor, although the negative deviation $D(t^2)$ is less marked than for α-Ga or for the BCS weak-coupling theory. It is of interest to estimate the energy gap $\Delta(0)$ for β-Ga. Our previous estimate[2] is too high, being based on the erroneous values of $D(t^2)$ and T_c. Using the empirical relationship of Toxen,[11] we find

$$\frac{2\Delta(0)}{kT_c} = \frac{2T_c}{H_0} \left.\frac{dH_c}{dT}\right|_{T_c} = 3.49 \simeq 3.5 \ .$$

This relationship is good to 2% for most elemental superconductors, with Nb and Hg as exceptions.

This estimate can be checked by using the formal BCS expression

$$2\Delta(0)/kT_c = \sqrt{\tfrac{1}{6}\pi}\ H_0/\sqrt{\gamma}\,T_c = 3.51 \simeq 3.5 \ .$$

Here, $\gamma = 1340\ \mathrm{erg/K^2\ cm^3}$ has been computed from our data on $H_c(T)$. (See Table I.) The BCS expression does not predict $\Delta(0)$ very accurately for real superconductors, but the two estimates taken together indicate that the energy gap in β-Ga lies close to the BCS value of 3.5. However, this energy gap does not agree with the tunneling results of Cohen *et al.*[12] They found that the phase which they identified as β-Ga had an energy gap $\Delta(0) = 1.03$ meV. With a transition temperature of 6.07 K, this yields $2\Delta(0)/kT_c = 3.9$.

In conclusion, we summarize the thermodynamic properties of superconducting β-Ga in Table I.

ACKNOWLEDGMENTS

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[4] ^{69}Ga of isotopic purity $(99.50 \pm 0.03)\%$, ^{71}Ga of isotopic purity $(99.61 \pm 0.03)\%$. This gives isotopic masses of 68.936 and 70.917, respectively.

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