Pressure Dependence of the Superconducting Transition Temperature
of dhcp and fcc Lanthanum

T. F. SMITH*

University of California, San Diego, La Jolla, California

AND

W. E. GARDNER

Atomic Energy Research Establishment, Harwell, England

The pressure dependence of the superconducting transition temperature of lanthanum has been extended from 10 to 40 kbar. The sample becomes predominantly fcc above 23 kbar. The superconducting transition temperature increases continuously up to 9°K, with a possible discontinuity at the phase change and a definite change of slope. The behavior in the fcc phase differs in sign with that predicted from thermal-expansion measurements at atmospheric pressure.

INTRODUCTION

IT has been observed[1] that applying pressure, up to a maximum of 10 kbar, raises the superconducting transition temperature T_c of dhcp (double hexagonal close packed) lanthanum from 5.5 to 7°K. Although this behavior is qualitatively consistent with the volume difference[2] between the normal and superconducting states of dhcp La below T_c, it contrasts strongly with a decrease in T_c with pressure observed in most other pure metal superconductors.[3] It is therefore of interest to determine whether T_c continues to increase with pressure, and we have made preliminary measurements extending the pressure range up to 40 kbar. This pressure range is associated with the transformation, at room temperature, from the dhcp phase to the fcc phase of lanthanum at approximately 23 kbar.[4-7] Since Andres[8] has observed that the volume difference of a fcc lanthanum specimen below T_c is opposite in sign to that of a dhcp specimen we anticipated that there would be a corresponding change of sign of the pressure dependence of T_c above 23 kbar.

MEASUREMENTS

The sample used in the present work was one of those used previously in the measurements up to 10 kbar. It was the sample obtained from the Lunex company and it was machined to fit a redesigned pressure cylinder. The pressure apparatus itself is based on the clamp design[9] and is basically the apparatus used in the measurements up to 10 kbar except for a cemented tungsten carbide (Kennametal $K6$) piston and cylinder. The tungsten carbide cylinder is supported in a collar of hardened Be-Cu alloy. The maximum pressure that could be achieved in this particular case was determined by the tungsten carbide cylinder. This was observed to fail at room temperature in attempting to obtain pressures above 40 kbar. At this pressure a number of cracks developed around its circumference but shattering of the carbide was prevented by the Be-Cu collar. A further limitation of this particular grade of tungsten carbide was associated with the occurrence of superconducting behavior between 3.5 and 4°K. This prevented the intended use of a superconducting tin manometer which had been incorporated to determine the pressure in the cylinder at low temperatures. The pressures quoted are, therefore, only nominal and may be in error by as much as $\pm 10\%$ in absolute value. Further measurements are planned in an apparatus constructed from a nonsuperconducting grade of tungsten carbide.
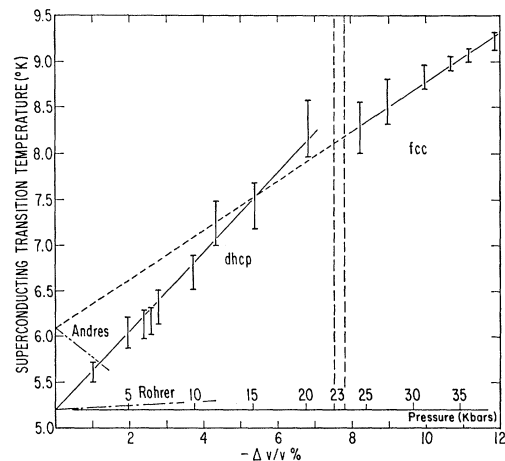
* Supported by the U. S. Air Force Office of Scientific Research.
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FIG. 1. The superconducting transition temperature of dhcp and fcc lanthanum as a function of % volume change.

RESULTS

The results obtained are presented graphically in Fig. 1, which is a plot of superconducting transition temperature against the % change in volume of the sample. The corresponding applied pressures are also indicated. The vertical bar associated with each point indicates the width of the transition when the rounding at the ends of the transition has been neglected. The points reproduced below 10 kbar are taken from the previous measurements.[1] The pressure values have been converted into the corresponding volume change by using the room-temperature-compressibility data of Bridgman.[4,10] This particular choice of abcissa has been made because the volume change is the more significant physical parameter.

The pressure associated with the phase change from dhcp → fcc is shown by the dashed lines at 23 kbar in Fig. 1. It can be seen that the results above 23 kbar do not show the anticipated decrease of T_c with pressure, but instead T_c continues to increase with applied pressure and in fact exceeds 9°K at 40 kbar. Furthermore, the value of T_c in both phases can be represented by a linear function of the change in volume with pressure. However, the slopes in the two phases are different and there appears to be a discontinuity in T_c associated with the phase change.[11] The apparent $\Delta T_c/\Delta V$ associated with the phase change is positive, in contrast to the negative values of $\partial T_c/\partial V$ in the two phases. It should also be noticed in Fig. 1 that the width of the transition decreases appreciably above 30 kbar, which suggests that the phase change is sluggish and has not been completed until this pressure is achieved.

DISCUSSION

One of the major problems involved in any interpretation of the results is the difficulty in making physical measurements on a single-phased sample of lanthanum. Since, normally, both dhcp and fcc phases are present in lanthanum at room temperature, it is necessary to heat-treat specimens appropriately in order to produce a single-phased sample.[12-14] Bearing

this in mind, from an examination of the literature it appears to us that the most reliable values for the superconducting transition temperatures of the dhcp phase and fcc phases are 4.9°K [13] and 6.06°K,[12,15] respectively.

From measurements of the volume change in the dhcp phase of lanthanum upon destroying superconductivity by the application of a magnetic field Rohrer[2] estimated the volume dependence of the superconducting transition temperature, which he quotes as $\partial \ln T_c/\partial \ln V \sim -0.5$. Using the quoted value of T_c for his particular specimen we have calculated $V\partial T_c/\partial V (\sim -2.3°K)$. This is shown as a broken line, labeled Rohrer, in Fig. 1.

From his low-temperature thermal expansion data on the fcc phase of lanthanum Andres[8] has estimated the volume difference between the normal and superconducting states at 0°K. From this estimated volume difference he has calculated the volume dependence of the superconducting transition temperature using the relationship [Eq. (33), Ref. 8]

$$(Vn - Vs)/Vn = -(\kappa H_0^2/8\pi)(\gamma_e + 2s),$$

where γ_e is the electronic Grüneisen constant, κ is the compressibility, and $s = \partial \ln T_c/\partial \ln V$. This thermodynamic relationship, derived from partial differentiation with respect to volume and temperature of the free-energy difference between the normal and superconducting states, embodies the assumption that the critical field curve is parabolic, i.e., $H_c = H_0(1 - (T/T_c)^2)$. Andres quotes the volume dependence of the superconducting transition temperature, calculated in this manner, as $\partial \ln T_c/\partial \ln V = 6.5 \pm 0.5$.

A more preferable procedure for calculating the volume dependence would be the direct application of Ehrenfest's equation

$$\left(\frac{\partial T_c}{\partial P}\right)_{T=T_c} = VT_c \frac{(\alpha_s - \alpha_n)}{(C_s - C_n)_{T=T_c}},$$

where V is the atomic volume and α and C are the thermal expansion coefficient and specific heat, respectively, in the superconducting (s) and normal (n) states. Strictly, such an application should only be made when both the specific heat and thermal expan-

[10] K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand Company, Inc., Princeton, New Jersey), p. 55.

[11] Though an extrapolation of the phase diagram (Ref. 5) of lanthanum to helium temperatures would indicate that the phase change at these temperatures would be in the region of 40 kbar, we do not believe that there will be any change in the state of the sample, which has been compressed at room temperature, on cooling, because of the sluggish nature of the reverse transition. (Refs. 5, 6). This assumption is supported by the recent work of T. R. R. McDonald, G. S. Barberich, and E. Gregory, American Society of Mechanical Engineers Report No. 64-WA/PT-4, 1964 (unpublished). which shows that the high-pressure fcc phase of Nd and Pr may be retained by quenching to 77°K before releasing the applied pressure.

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[13] D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Speddding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965).

[14] Predominantly dhcp samples were obtained by wrapping the

lanthanum in tantalum foil (used to reduce oxidation during the long anneal) and annealing in a vacuum furnace which was allowed to fall in temperature from 260 to 180°C over a period of a week. The sample was then allowed to return to room temperature in a few hours. Neutron-diffraction measurements on samples given this treatment showed that they contained more than 95% of the dhcp phase. Fcc samples were heated for 24 h at 400°C in a vacuum furnace ($\sim$5$\times$10^{-6} mm Hg). The furnace was then slowly brought to atmospheric pressure at 400°C with pure argon gas. Finally the sample was quenched by dropping it from the furnace into iced brine. Neutron-diffraction measurements showed that such samples contained only 85% of the fcc phase. Leslie *et al.* state that they have achieved 95% fcc samples in thin plates by a similar heat treatment, whereas we were unable to improve appreciably the above fcc content.

[15] T. Mamiya, T. Fukuroi, and S. Tanuma, J. Phys. Soc. Japan **20**, 1559 (1965).

sion data have been taken on the same sample. However, utilization of data from different samples of sufficiently high purity should not lead to serious error. Unfortunately, such an application may not be strictly valid for lanthanum because of the two-phase nature of the samples for which data are available. However, it is still of interest to compare the value obtained by this procedure with that of Andres. We have attempted to re-interpret Andres expansion results to obtain $(\alpha_s-\alpha_n)_{T=T_c}$ by plotting $\Delta l/T^2$ against T^2, where l is the sample length. We find an anomalous behavior between 4.5 and 6°K (which is indicative of a two-phased sample as suggested by Andres) and there is also an anomalous change of slope in the normal phase at about 8°K. Consequently we have only obtained a rather crude value for the discontinuity in the expansion coefficient at $T=T_c$. In addition, as no satisfactory specific heat data on a fcc specimen have been published we have been obliged to make use of the data of Berman et al.[16] on a two-phase specimen to estimate C_s-C_n. Using these values we have calculated $\partial \ln T_c/\partial \ln V \sim 4.3$ using a room temperature compressibility[17] of 4.2×10^{-6} bar^{-1}. This value is in reasonable agreement, considering the uncertainties involved, with that of Andres'. Better agreement is obtained if we substitute our chosen value for the compressibility for the lower value used by Andres. We calculate the slope $V\partial T_c/\partial V$ to be between 27 and 38°K, and this is also shown, as a broken line labeled "Andres," in Fig. 1. It should be emphasized that although there is some uncertainty about the slope of this line, there is no uncertainty about its sign.

Our observations can be compared with this predicted behavior in Fig. 1. It can be seen that our results in the dhcp phase are best represented by a line which intersects the $P=0$ axis at 5.2 ± 0.1°K. This value is somewhat higher than the selected best value $(4.9°K)$.[13] Furthermore, the zero-pressure superconducting transition temperatures following the application of pressure were consistently higher $(5.5\pm0.1°K)$ than this extrapolated value. This is presumably associated with the sensitivity of T_c to strain in the sample.

From our observed value of $V(\partial T_c/\partial V)(-43\pm4°K)$, in the dhcp phase, we have calculated a value of $\partial T_c/\partial P$ of $19\pm2\times10^{-5}$ °K bar^{-1} at $P=0$ from the initial compressibility $(4.2\times10^{-6}$ bar$^{-1})$.[4,10] This value is somewhat larger than the value given previously,[1] and only qualitatively agrees with the value, $\sim1\times10^{-5}$ °K bar^{-1}, deduced from the data of Rohrer.[2]

The best line through the results in the fcc phase intersects the $P=0$ axis at 6.1 ± 0.1°K in good agreement with the best value[12,15] of T_c. The corresponding value of $V(\partial T_c/\partial V)$ is -27 ± 1.5°K. Using a com-

pressibility value of 4.2×10^{-6} bar^{-1} we calculate $\partial T_c/\partial P=11.3\pm0.6\times10^{-5}$ °K bar^{-1} at $P=0$ compared with a value of $-13\pm2\times10^{-5}$ °K bar^{-1} from the data of Andres.[8]

We may attempt to obtain an explanation for this observed behavior in the fcc phase of lanthanum by considering the volume derivative of the simple BCS[18] relationship,

$$T_c=0.85\Theta_D\exp(-1/A),\qquad(1)$$

with $A=N(0)J$, where $N(0)$ represents the density of electron states at the Fermi surface and J represents the attractive electron-electron interaction parameter. We may express the volume derivative as

$$\frac{\partial \ln T_c}{\partial \ln V}=\ln\left(\frac{0.85\Theta_D}{T_c}\right)\varphi-\gamma_G\sim3\varphi-1.2,\qquad(2)$$

where $\varphi=\partial \ln A/\partial \ln V$ and γ_G is the Grüneisen constant representative of the volume dependence of the phonon spectrum.[8] We have previously[19] discussed the sign of φ consistent with the observed pressure dependences in superconducting elements. In the present case, for the fcc phase of lanthanum, we observe a value of $\partial \ln T_c/\partial \ln V$ of -4.5 for pressures greater than 23 kbar, whereas we deduce a value at atmospheric pressure of 4.3–6.5 from the data of Andres.[8] We conclude, therefore, that the only way that these contrasting values of φ may be reconciled is by a reversal of sign of φ as the volume is decreased.

Now attempts[20,21] have been made to relate the value of φ to its two constituents, namely $\partial \ln N(0)/\partial \ln V$ and $\partial \ln J/\partial \ln V$, since $\partial \ln N(0)/\partial \ln V$ can be determined experimentally from thermal expansion measurements and from the pressure dependence of critical magnetic field measurements. For non-transition metal superconductors, where (1) is a reasonable approximation, $\partial \ln N(0)/\partial \ln V$ varies widely from the free-electron value of $\frac{2}{3}$ and it is necessary to adjust both the sign and magnitude of $\partial \ln J/\partial \ln V$ to obtain numerical agreement with the observed values of φ. In view of the absence of any consistent behavior in the simpler case of the nontransition metal superconductors, there appears to be little hope, at present, of a simple understanding of the form of $\partial \ln A/\partial \ln V$ in the transition metal superconductors with their more complex form of A.[22–24] Since we are at present unable

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[17] The initial compressibility of the fcc form is not known but an inspection of the compressibility curve (Ref. 4) suggests it would be roughly the same as the value in the dhcp form $(4.2\times10^{-6}$ bar$^{-1})$.

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to relate φ to its constituents we cannot even attempt to explain this observed change of sign with volume.

Finally, it is possible that if measurements could be made on the fcc phase at pressures below 23 kbar it would be observed that T_c first decreases with applied pressure and then increases. We think that very pure fcc samples would be required in order to make useful observations of this kind. However, as the "pure" fcc phase of lanthanum readily converts to a mixture of the dhcp and fcc phases at room temperature

upon even slight straining[18] there seems to be little hope of conducting such measurements. Instead we would prefer to see a repeat of the thermal-expansion measurements of Andres on fcc lanthanum in order to confirm the present interesting situation.

ACKNOWLEDGMENTS

We should like to thank K. Andres, H. London, and L. J. Sham for a number of informative discussions.

New Relationship for Superconductors

J. Grunzweig-Genossar and M. Revzen

Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel

(Received 20 January 1966)

A relationship between the energy gap of superconductors at zero temperature and the slope of the critical magnetic field at the critical temperature is presented. Thermodynamical argument gives the dependence of this relationship on the electronic specific heat near the critical temperature and an approximate formula for the latter is proposed. The conclusions are compared with experimental data.

I. INTRODUCTION

RECENTLY, Toxen[1] proposed a relationship between the energy gap of superconductors at zero temperature $[\Delta(0)]$ and the slope of the critical magnetic field at the critical temperature (T_c). Toxen showed, for example, that BCS[2] theory (in the weak-coupling limit) satisfies his relation. It was pointed out[3] that the Toxen relationship is, probably, a numerical coincidence. In this paper we amplify the argumentation which is given in Ref. 3. Thus the thermodynamics of Lewis's[4] model is given (without recourse to the two-fluid model) in Sec. II.

We discuss the experimental aspects of the problem in Sec. III and mention explicitly the experimental results which are useful in discriminating between the Toxen relation and the curve of Ref. 3.

II. THERMODYNAMIC DERIVATION OF LEWIS' FORMULA

Lewis[4] derived a relationship between a parameter (α) appearing in an approximate formula for the specific heat of supercondutors (C_s), and the slope of the critical field at the critical temperature. Lewis' derivation (as are those of Refs. 5 and 6) is associated

with the two-fluid model for superconductors. We shall outline a thermodynamic derivation of the results without recourse to the two-fluid model. A more general formula—for arbitrary specific-heat curve—is also given. It is valid for superconductors which show the Meissner effect.

In what follows we make the usual assumptions with regard to the separability of the electronic and lattice contributions, and also assume that the latter is unaffected by the transition to the superconducting state. These assumptions are listed and discussed, for example, in Ref. 7.

The electronic specific heat for the superconductor is approximated[4] in the vicinity of T_c:

$$C_s/\gamma T_c = Ae^{-\alpha(T_c/T)}, \quad T < T_c. \tag{1}$$

Here T is the temperature and γ is given by the electronic specific heat of the normal metal (C_n) at low temperatures, i.e.

$$C_n = \gamma T.$$

Our problem here is to eliminate A and γ in terms of other quantities. At T_c the entropies of the two phases, superconducting and normal, are equal,[4] viz.

$$\int_0^{T_c} C_s \frac{dT}{T} = \gamma T_c,$$

or

$$AE(\alpha) = 1, \tag{2}$$

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