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

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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.

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INTRODUCTION

It has been observed[1] that applying pressure, up to a maximum of 10 kbar, raises the superconducting transition temperature (T_c) of hcp 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 hcp 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 hcp phase to the fcc phase of lanthanum at approximately 23 kbar.[4-8] Since Andres[9] has observed that the volume difference of a fcc lanthanum specimen below T_c is opposite in sign to that of a hcp 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 re-designed pressure cylinder. The pressure apparatus itself is based on the clamp design[10] 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 ± 10% in absolute value. Further measurements are planned in an apparatus constructed from a non-superconducting grade of tungsten carbide.

RESULTS

The results obtained are presented graphically in figure 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.[4,11] 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 hcp → fcc is shown as the dashed lines at 23 kbar in figure 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.[12] It should also be noticed in figure 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. This is in agreement with the results of previous investigations at room temperature.[4-8]

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 hcp 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.[13,14,15] 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 hcp phase and fcc phases are $4.9^{\circ}K$[14] and $6.06^{\circ}K$[13] respectively.

From measurements of the volume change in the hcp 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 $v\partial T_c/\partial v$ ($\sim -2.3^{\circ}K$). This is shown as a broken line, labelled Rohrer, in figure 1.

From his low temperature thermal expansion data on the fcc phase of lanthanum Andres[9] has estimated the volume difference between the normal and superconducting states at $0^{\circ}K$. From this estimated volume difference he has calculated the volume dependence of the superconducting transition temperature, which he quotes 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. We have attempted to re-interpret Andres expansion results to obtain

$$(\alpha_s - \alpha_n)_{T=T_c}$$

by plotting $\Delta\ell/T^2$ 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 a 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[16] et al on a two phase specimen to estimate $C_s - C_n$. Using these values we have calculated $\partial \ln T_c/\partial \ln v \sim 4.3$ which is in reasonable agreement, considering the uncertainties involved, with Andres' value. We calculate the slope $v\partial T_c/\partial v$ to be between 27-38°K, and this is also shown, as a broken line labelled Andres, in figure 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 figure 1. It can be seen that our results in the hcp 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).[14] Furthermore the zero pressure superconducting transition temperatures

following the application of pressure were consistently higher ($5.5 \pm 0.1^{\circ}K$) than this extrapolated value. This is presumably associated with the sensitivity of T_c to strain in the sample.

From our observed value of $V\frac{\partial T_c}{\partial V}$ ($-43 \pm 4^{\circ}K$), in the hcp phase, we have calculated a value of $\frac{\partial T_c}{\partial P}$ of $19 \pm 2 \times 10^{-5}\ ^{\circ}kbar^{-1}$ at P = 0 from the initial compressibility ($4.2 \times 10^{-6} bar^{-1}$).[4,11] This value is somewhat larger than the value given previously,[1] and only qualitatively agrees with the value, $\sim 1 \times 10^{-5}\ ^{\circ}kbar^{-1}$, deduced from the data of Rohrer.[2]

The best line through the results in the fcc phase intersects the P = 0 axis at $6.1 \pm 0.1^{\circ}K$ in good agreement with the best value[13] of T_c. The corresponding value of $V\frac{\partial T_c}{\partial V}$ is $-27 \pm 1.5^{\circ}K$. The initial compressibility of the fcc form is not known but an inspection of the compressibility curve[4] suggests it will be roughly the same as the value in the hcp form ($4.2 \times 10^{-6} bar^{-1}$). Using this value we calculate $\frac{\partial T_c}{\partial P} = 11.3 \pm 0.6 \times 10^{-5}\ ^{\circ}kbar^{-1}$ at P = 0, compared with a value of $-13 \pm 2 \times 10^{-5}\ ^{\circ}kbar^{-1}$ from the data of Andres.[9]

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[17] 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,

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

$$\sim 3\varphi - 1.2$$

where $\varphi = \frac{\partial \ln A}{\partial \ln V}$ and γ_G is the Grüneisen constant representative of the volume dependence of the phonon spectrum. We have previously[18] discussed the sign of φ consistent with the observed pressure dependences in super-

conducting elements. In the present case, for the fcc phase of lanthanum, we observe, a value of $\frac{\partial \ln T_c}{\partial \ln V}$ 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.[9] We conclude, therefore, that the only way that these contrasting values of Ψ may be reconciled is by a reversal of sign of ψ as the volume is decreased.

Now attempts[19,20] have been made to relate the value of Ψ to its two constituents, namely $\frac{\partial \ln N(0)}{\partial \ln V}$ and $\frac{\partial \ln J}{\partial \ln V}$, since $\frac{\partial \ln N(0)}{\partial \ln V}$ 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, $\frac{\partial \ln N(0)}{\partial \ln V}$ varies widely from the free electron value of 2/3 and it is necessary to adjust both the sign and magnitude of $\frac{\partial \ln J}{\partial \ln V}$ to obtain numerical agreement with the observed values of Ψ. In view of the absence of any consistent behavior in the simple case of the non-transition metal superconductors, there appears to be little hope, at present, of a simple understanding of the form of $\frac{\partial \ln A}{\partial \ln V}$ in the transition metal superconductors with their more complex form of A.[21-23] Since we are at present unable to relate Ψ 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 hcp and fcc phases at room temperature upon even slight straining 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.

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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 hcp phase. Fcc samples were heated for twenty-four hours 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 their plates by a similar heat treatment, whereas we were unable to improve appreciably the above fcc content.

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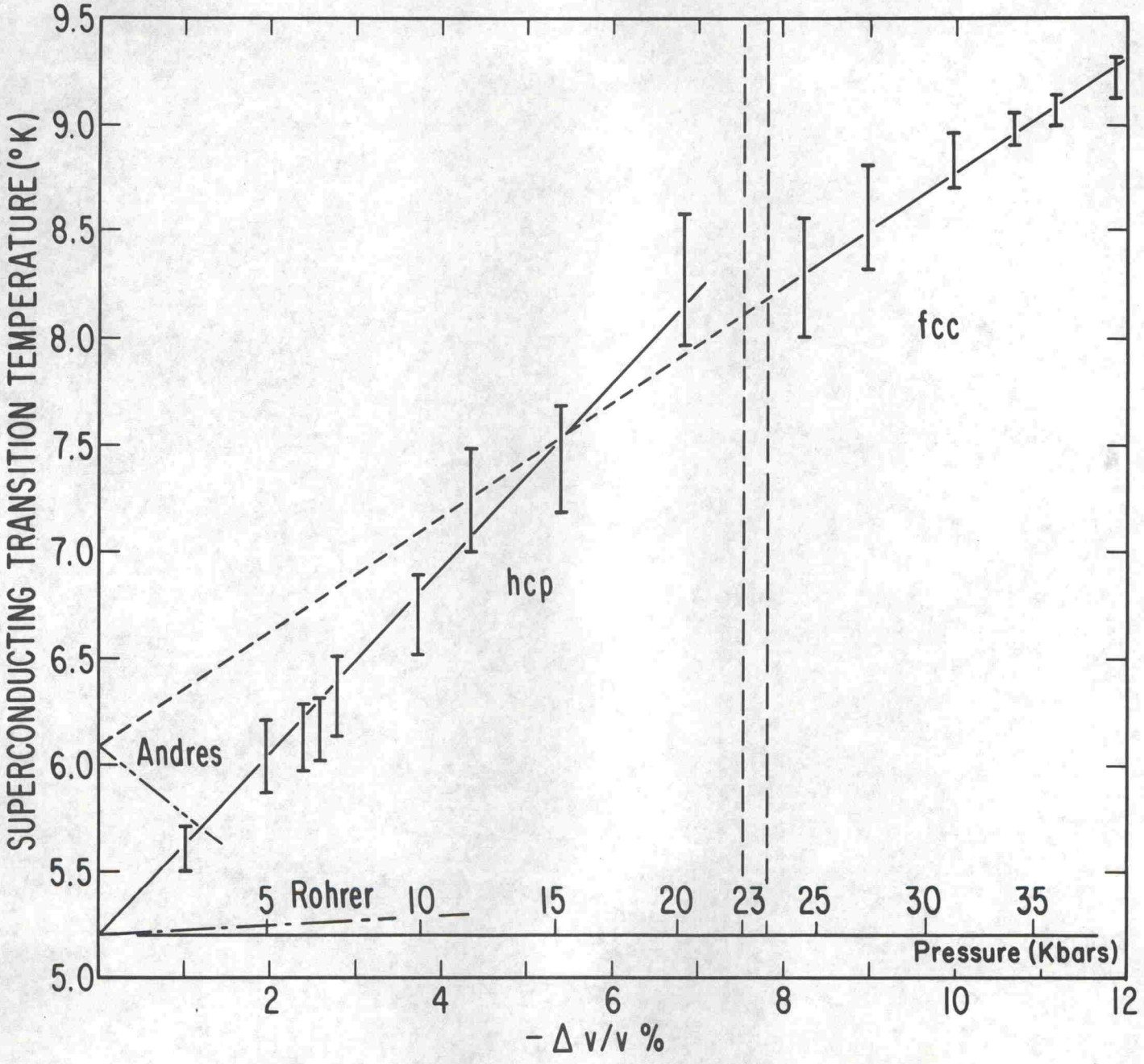
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FIGURE CAPTION

Fig. 1 The superconducting transition temperature of hcp and fcc lanthanum as a function of % volume change.


SUPERCONDUCTING TRANSITION TEMPERATURE (°K)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
fcc
hcp
Andres
Rohrer
5
10
15
20
23
25
30
35
Pressure (Kbars)
2
4
6
8
10
12
- Δ v/v %