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Heat capacity in superconducting and normal-state LaS_x $(1.333 \leq x \leq 1.500)$ compounds

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The low-temperature heat capacity of the superconducting LaS_x $(1.333 \leq x \leq 1.500)$ compounds with the Th_3P_4-type structure were measured from 1.3 to 20.0 K in magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T. The compositional variation of the electronic specific-heat parameter γ and the Debye temperature Θ_D in LaS_x are discussed in connection with the electric properties of these alloys. The results also show that the LaS_x alloys near $x = 1.333$ are strong-coupling type-II superconductors having large values of the electron-phonon coupling constant values, $\lambda = 0.71$, and upper critical field values of $H_{c2}(0)$, e.g., 16.2 T for $LaS_{1.366}$. The $LaS_{1.346}$ and $LaS_{1.355}$ alloys undergo a cubic-to-tetragonal phase transition at 85 and 55 K, respectively. The former composition has the intrinsic coherence length ξ_0 of 158 Å, which gives a large value for the intrinsic Ginzburg-Landau parameter, $\kappa_0 = 11$. However, this tetragonal phase, which forms only in the narrow composition region of $1.333 \leq x \leq 1.362$, has a lower γ value than the cubic-phase alloys with $x \simeq 1.37$. Furthermore, the superconducting transition temperatures of LaS_x compounds hardly have any compositional variation for $x \leq 1.36$. Finally, there is a large drop in $H_{c2}(0)$ from 16.2 T for the cubic phase at $x = 1.366$ to 9.7 T for the tetragonal phase at $x = 1.346$. This study also clearly illustrates that lattice instability is an important factor governing the superconducting behavior of these alloys, but the best superconducting properties are found in the stable phase (bcc) just before it becomes unstable, rather than in the phase which actually undergoes the transformation.

I. INTRODUCTION

The superconductivity of the γ-phase "La_3S_4" compound was found by Bozorth *et al.*[1] and Guthrie and Palmer[2] to have a superconducting transition temperature T_c of 8.25 K. These LaS_x compounds of γ phase have the bcc Th_3P_4 type structure and a wide single phase region between $x = 1.333$ and 1.500 at room temperature. The lattice parameter does not change with composition ($a = 8.730$ Å for $x = 1.333$ and $a = 8.731$ Å for 1.500),[3] although there are vacancies at the lanthanum sites for compositions of $x > 1.333$.[4] The $LaS_{1.500}$ compound, which has a vacancy concentration of $\frac{1}{9}$ at the lanthanum sites, is semiconducting and the electrical properties of LaS_x compounds change from metallic to semiconducting with increasing sulfur concentrations.[2,5]

Concerning the electrostatic stability of these compounds, Carter[6] has proposed the vacancy and charge ordering model. From x-ray powder diffraction experiments, however, Dernier *et al.*[7] have found that the "La_3S_4" compound undergoes a cubic to tetragonal phase transformation, T_M, below 90 K. They have concluded that the largest value of lattice parameter ratio c/a in the tetragonal phase is only 1.010 and the phase transition is of first order, which casts some doubt on the charge order-disorder mechanism proposed by Carter.[6] On the other hand, Shelton *et al.*[8] have reported that both T_c and this crystallographic transformation temperature rise with increasing pressure in "La_3S_4," and Bucher *et al.*[9] discussed the high superconducting transition temperature of this compound to be associated with a softening in certain lattice modes.

While our work was in progress, Westerholt *et al.*[10] have recently reported that the "La_3S_4" compound is a strong coupling superconductor with a coherence length of 132 Å from the electrical resistivity, specific heat at zero field and magnetization measurements. They have found that this compound is a superconductor having a high upper critical field $H_{c2}(T)$. And more recently while in the final stages of writing this manuscript they have published a series of papers giving more details of their study on the La_3S_4-La_2S_3 alloys.[11–13] These results include additional magnetic susceptibility and zero field heat-capacity values as a function of x (LaS_x),[11] elastic constant measurements,[12] and low-temperature x-ray lattice parameters.[13] In general their results are in reasonable agreement with our results for T_c, T_M, γ, Θ_D, and $H_{c2}(0)$, except for a shift in the chemical compositional dependences of these quantities. This apparent discrepancy will be discussed later.

The "La_3S_4-La_2S_3" alloy seems to be an ideal system in which to investigate the relationship between the superconducting properties of a solid and not only the normal-state properties but also the lattice instability. We have, therefore, systematically measured the low-temperature heat capacity of LaS_x from $x \cong 1.333$ to 1.500 in magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T, and checking whether or not a sample underwent a crystallographic transformation by electrical resistivity measurements between 4.2 and 300 K. We have briefly reported[14] that this cubic to tetragonal transformation, which arises only in the narrow composition region of $1.333 \leq x \leq 1.362$, has a large effect on the electronic specific-heat constant γ and the upper critical field $H_{c2}(0)$ values, but hardly any effect on T_c.

In the present paper, the experimental results of low-temperature (1.3 to 20 K) heat capacity are reported in detail and the nature of superconductivity of these compounds having high T_c near $x = 1.333$ is discussed in connection with their electronic properties and the crystallographic transformation.

II. EXPERIMENTAL

A. Sample preparation

The lanthanum used in this investigation was prepared in this laboratory by the calcium reduction of lanthanum fluoride followed by a vacuum casting of the lanthanum. The major impurities in *atomic parts per million* of the lanthanum material (all other impurities are present at 1 atomic ppm or less) are H(275), C(128), N(30), O(295), F(146), Cl(3), Fe(10), Ni(2), Cu(10), Nb(< 3), Gd(< 7), and Ta(3.4). The sulfur, which was specified to be 99.999% pure, was obtained from American Smelting and Refining Company.

The LaS_x samples used in the specific-heat measurements were prepared by direct combination of La and S between 600 and 900 °C in sealed quartz capsules, and followed by melting in a tungsten crucible under an argon atmosphere in an induction furnace. To ensure homogeneity, all LaS_x ingots prepared were annealed at 1700 °C for 4 h and then quickly cooled. This heat treating procedure resulted in a sharp superconducting peak in the C/T vs T^2 curves and the resulting values of γ and the Debye temperature Θ_D differ from our previous preliminary zero field data,[15] which were measured on melted but unannealed samples. The final compositions of our LaS_x samples were determined by chemical analyses. The chemical analyses were made by first dissolving the samples in $4.8M$ hydrochloric acid. The lanthanum content was determined by titrating this solution with EDTA (ethylene diamine tetraacetic acid) which had been freshly standardized against a pure lanthanum metal sample dissolved in hydrochloric acid. The titration was done at a pH of 5.5 with xylenol orange as the indicator. The sulfur content was obtained by subtracting from 100%. The precision of the chemical analysis are within ± 0.002 in $x(LaS_x)$.

In order to determine whether or not a crystallographic transformation occurred in the samples studied, all LaS_x samples used in the specific-heat measurements were checked by measuring the electrical resistivity between 4.2 and 300 K.[16] We have found that the crystallographic transformation occurs without any thermal hysteresis in the narrow composition region $1.333 \leq x \leq 1.362$.

B. Thermometer calibration

An isolation heat-pulse type low-temperature calorimeter with a mechanical heat switch was used in this work. The temperature was measured by a Cryo Cal-5012 germanium resistance thermometer (GRT) and the GRT calibration under magnetic fields was carried out in this calorimeter in the following manner. The desired temperature was achieved either by using a heater after the mechanical heat switch was opened above 4.2 K, or by changing the vapor pressure over liquid helium in the inner pot after the switch was closed below 4.2 K. A thermally isolated condition of the addenda at the desired temperature was attained by using a slight heater current (0.01–1 μA) above 4.2 K and a manostat below 4.2 K. Under this isolating condition, the resistance of the GRT was measured at the desired temperature in zero and magnetic fields of 2.50, 5.39, 7.62, and 9.98 T, which were produced by a superconducting magnet, and then again at zero field before changing temperature. A sufficiently long time was used to make the measurements to avoid increasing the temperature of the addenda due to changing magnetic fields.

In this way, 32 to 34 data points were obtained for each magnetic field. The resistance R versus tem-

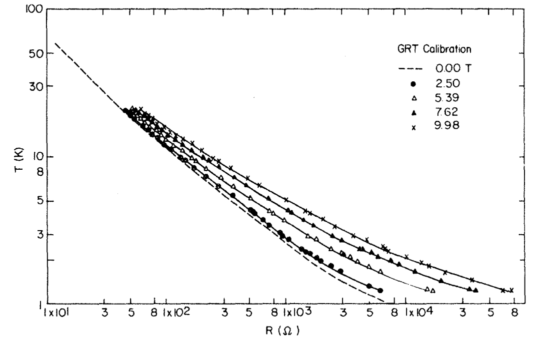

FIG. 1. GRT calibration results at five magnetic fields. The solid lines through the data points are the results of the least-square fits. The dashed line is the GRT calibration results in zero field.

perature T values were fitted by means of a least-square technique of the form[17,18]

$$\ln T = \sum_{i=0}^{8} A_i (\ln R)^i \ , \tag{1}$$

where $A_i (i = 0-8)$ are fitting constants. Figure 1 shows the results of the GRT calibration in four magnetic fields.

C. Heat-capacity measurements

The addenda, which consists of a copper sample holder, a 2.2-kΩ Pt-W wire heater, GRT and a strontium titanate capacitance sensor, was calibrated by measuring the heat capacity C at zero and four magnetic fields. The results were fitted by means of a least-square technique of the form

$$C = \sum_{i=1}^{6} B_i T^{2i-1} \tag{2}$$

over narrow temperature ranges of 1.3 to 1.6, 1.6 to 2.2, 2.2 to 4.2, 4.2 to 8.0, and 8.0 to 20.0 K.

In order to check the GRT calibration and the heat-capacity data of the addenda, the heat capacity of a Calorimetry Conference copper standard sample[17] was measured between 1.3 and 20.0 K. The results of the heat-capacity measurements for Cu at zero and the four magnetic fields were fitted in the temperature range between 1.3 and 5.0 K by a least-squares technique using an equation of the form

$$C/T = \gamma + \beta T^2 \ , \tag{3}$$

where

$$\beta = 1944/\Theta_D^3 \ \text{(J/g atom K}^4) \ . \tag{4}$$

The resulting γ values ranged from 0.676 to 0.689 mJ/g atom K^2 and the Θ_D values ranged from 335 to 348 K. Both values agree within ~2% of the previous zero field data.[17,19]

In order to avoid trapping magnetic flux in the superconducting sample,[20] all measurements from 1.3 to 20.0 K in magnetic fields were performed in the following way. The sample was cooled down to 1.3 or 4.2 K in zero field, after which the desired magnetic field was applied slowly so that the temperature of the sample did not rise above T_c. Sufficient time was allowed to cool the sample after attaining the desired magnetic field before the heat-capacity measurements were made at a particular field. Before the next set of data were taken, the field was reduced to zero and the sample was heated to just above T_c. Then the sample was cooled again in zero field and the desired magnetic field applied.

III. RESULTS

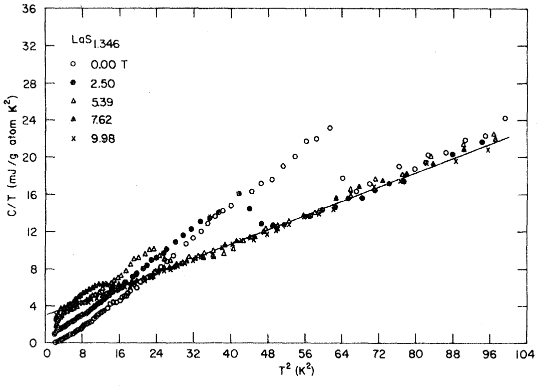

FIG. 2. Heat capacity of $\mathrm{LaS}_{1.346}$ at five magnetic fields.

The heat-capacity measurements were made between 1.3 and 20.0 K for five superconducting LaS_x specimens of $x = 1.346$, 1.355, 1.366, 1.399, and 1.433 at magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T, and for two nonsuperconducting specimens, $\mathrm{LaS}_{1.456}$ and $\mathrm{LaS}_{1.496}$, in zero field only. Figures 2–7 show the C/T vs T^2 plots for the seven compositions. The temperature at which superconductivity begins, T_c^*, and the midpoint transition temperature T_c are summarized in Table I. For $\mathrm{LaS}_{1.355}$ and $\mathrm{LaS}_{1.366}$ (Figs. 3 and 4) the presence of a superconducting peak is evident at 9.98 T, while the superconducting peak in the C/T vs T^2 curves is observed at fields of 0 to 7.62 T for $\mathrm{LaS}_{1.346}$ and $\mathrm{LaS}_{1.399}$ (Figs. 2 and 5) and at 0 and 2.50 T for $\mathrm{LaS}_{1.433}$ (Fig. 6). Both the $\mathrm{LaS}_{1.456}$ and the $\mathrm{LaS}_{1.496}$ are not superconducting down to 1.2 K and the C/T vs T^2 plots are linear below ~7 K (Fig. 7).

The normal-state portions of all C/T vs T^2 curves were analyzed by using Eq. (3). Values of γ and Θ_D were obtained by a least-squares fit of the data at zero and the four magnetic fields, see Table I. A further check on the reliability of the γ and Θ_D values, especially for the first three samples where extrapolations were made from above 4 K, was obtained from the entropy calculations from 0 to T_c^* for

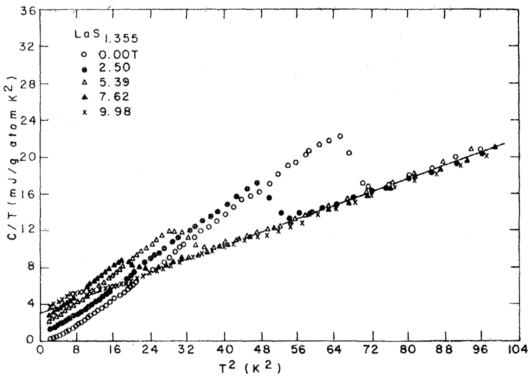

FIG. 3. Heat capacity of $\mathrm{LaS}_{1.355}$ at five magnetic fields.

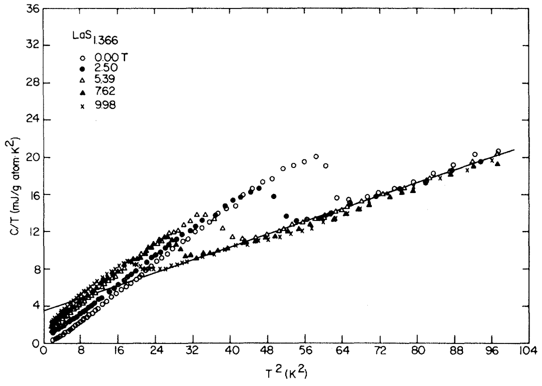

FIG. 4. Heat capacity of $LaS_{1.366}$ at five magnetic fields.

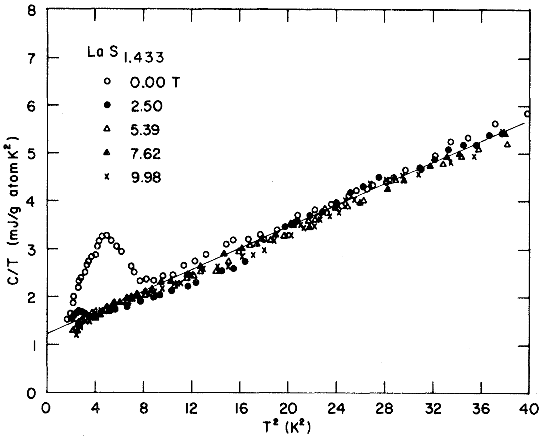

FIG. 6. Heat capacity of $LaS_{1.433}$ at five magnetic fields.

both the normal and superconducting states. The resultant entropies agreed within 2% indicating that γ and Θ_D values obtained from these extrapolations are valid. The solid lines in Figs. 3–7 are the results of a least-squares fit of the data.

The electronic specific heat in superconducting state C_{es} can be determined from the relation $C_{es} = C_s - C_n + \gamma T$, if the difference of lattice specific heat between superconducting and normal states is negligible. The Bardeen-Cooper-Schrieffer (BCS) theory[21] predicts

$$\frac{C_{es}}{\gamma T_c} = a \exp\left(-b\frac{T_c}{T}\right) , \tag{5}$$

where a and b, respectively, are 8.5 and 1.44 over the range $2.5 < T/T_c < 6$. As shown in Fig. 8, the experimental values are in poor agreement with theory except possibly for $LaS_{1.433}$. Because of this disagreement we have analyzed our data in terms of the modified BCS theory for strongly coupled superconductors in which the temperatures dependence of the energy gap, $\Delta(0)$, is given by the BCS functional form, but $\Delta(0)$ is a fitted parameter [i.e., $\Delta(T)/\Delta^{\mathrm{BCS}}(T) = \mathrm{const}$].[22] The values of the energy gap, which are given as $2\Delta(0)/kT_c$ (obs) in Table II were obtained from C_{es} for the range $1.5 < T_c/T < 4$ and are larger than the BCS prediction of 3.53 with the exception of $LaS_{1.433}$, which is slightly smaller. Table II also shows the a and b values estimated from Fig. 8 and the reduced jump in zero field heat capacity at T_c, $\Delta C/\gamma T_c$, for the superconducting LaS_x compounds. The $LaS_{1.346}$ and $LaS_{1.355}$ alloys with the tetragonal structure have a larger a value than the BCS prediction of 8.5. The value of $\Delta C/\gamma T_c$ also is considerably larger than the BCS prediction of 1.43 especially for alloys which transform to the tetragonal phase.

The thermodynamic critical field $H_c(T)$ can be

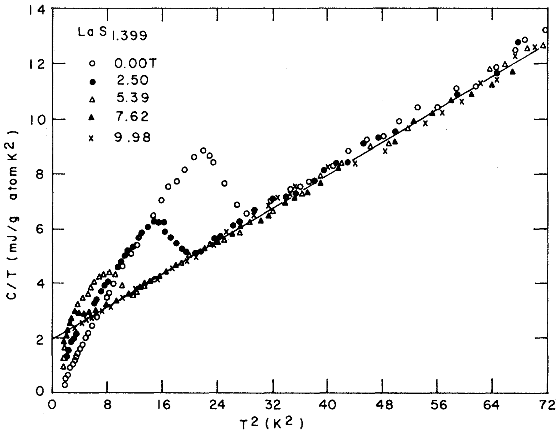

FIG. 5. Heat capacity of $LaS_{1.399}$ at five magnetic fields.

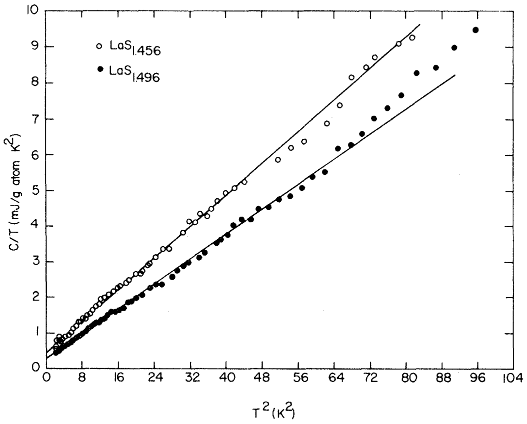

FIG. 7. Heat capacity of $LaS_{1.456}$ and $LaS_{1.496}$ at zero field.

TABLE I. Results of heat-capacity measurements; the electron-phonon coupling parameter (λ); and the electronic density of states at the Fermi surface [$N(0)$] for the LaS_x compounds.

x	T_c (K)	T_c^* (K)	$\Delta(T_c)$ (K)	γ $\left(\frac{mJ}{g\ at.\ K^2}\right)$	β $\left(\frac{mJ}{g\ at.\ K^4}\right)$	Θ_D (K)	λ	$N(0)$ $\left(\frac{states}{eV/at.}\right)$	Temp. range of fit (K)
1.346	7.97	8.30	0.33	3.01	0.190	217	0.73	0.738	4.1– 8.0
1.355	8.29	8.65	0.36	2.98	0.183	220	0.74	0.726	5.0–10.0
1.366	7.87	8.24	0.37	3.56	0.172	224	0.71	0.883	5.0–10.0
1.399	5.01	5.35	0.34	1.92	0.149	236	0.58	0.515	2.0– 7.0
1.433	2.61	2.90	0.29	1.22	0.112	259	0.46	0.354	1.9– 5.5
1.456	0.208[a]	. . .	. . .	0.47	0.110	261	0.29	0.155	1.8– 5.0
1.496	< 0.06[a]	. . .	. . .	0.30	0.087	282	. . .	0.127	1.3– 5.0

[a] Measured by C. Hamaker and M. B. Maple, University of California, San Diego, Calif.

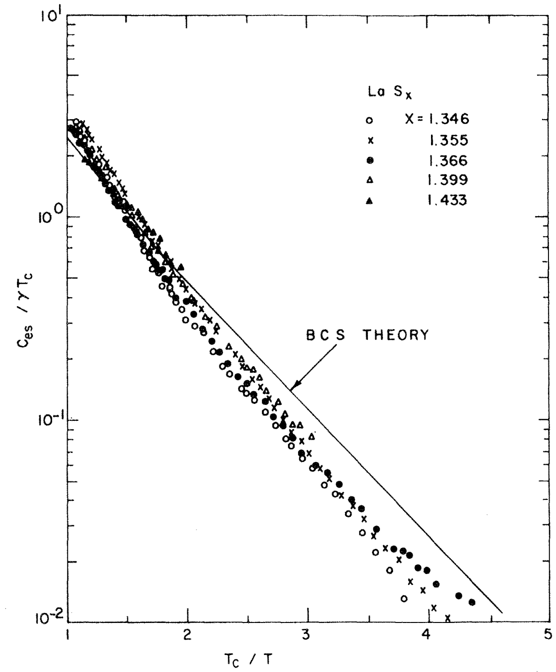

FIG. 8. Reduced superconducting electronic specific heat of LaS_x compounds. The solid curve is that predicted by the BCS theory.

determined by the relationship[23]

$$G_N(T) - G_S(T) = \int_T^{T_c} [S_N(T) - S_S(T)]dt$$
$$= \left[\frac{V}{8\pi}\right][H_c(T)]^2 \ . \qquad (6)$$

The entropy $S_i(T) = \int_0^T [C_i(T)/T]dT$ was obtained by measuring the area under the curve on a large scale graph of $C_i(T)/T$ vs T, where i denotes the normal (N) or the superconducting (S) state.

At T_c the total entropy in the normal state was found to be equal to the total entropy in the superconducting state within 2%. This result agrees with the prediction of the third law of thermodynamics within experimental error. Using the values of the entropy difference, Eq. (6) was integrated graphically and the $H_c(T)$ values were obtained by using the molar volume V given in Table II. The critical fields at $T=0$ are also shown in Table II. As seen in Fig. 9, one finds that the $H_c(T)$ values for all specimens fit the relation[23]

$$H_c(T) = H_c(0)(1-t^2) \ , \qquad (7)$$

where $t \equiv T/T_c$. It is seen that the thermodynamic critical field increases with decreasing x (increasing lanthanum content) until a value of $x \cong 1.36$ is reached and then $H_c(T)$ remains essentially constant for $x = 1.36$ to 1.34.

TABLE II. Molar volume V, thermodynamic critical field at 0 K [$H_c(0)$]; jump in the heat capacity at $T_c(\Delta C)$; reduced energy gap [$2\Delta(0)/kT_c$]; the parameters a and b from the reduced superconducting state electronic heat-capacity expression Eq. (5); and the measured value of the reduced jump in the heat capacity at $T_c(\Delta C/\gamma T_c)$ for the superconducting LaS_x compounds.

x	V (cm^3/g at.)	$H_c(0)$ (T)	ΔC(calc) $\left[\frac{\text{mJ}}{\text{g at. K}}\right]$	ΔC(obs) $\left[\frac{\text{mJ}}{\text{g at. K}}\right]$	$\frac{2\Delta(0)}{kT_c}$(calc)	$\frac{2\Delta(0)}{kT_c}$(obs)	a	b	$\frac{\Delta C}{\gamma T_c}$
1.346	14.368	0.101	58.8	57.0	4.02	4.09	9.4	1.67	2.38
1.355	14.409	0.104	59.7	57.0	3.99	4.03	9.6	1.64	2.30
1.366	14.458	0.104	63.0	53.0	3.84	3.87	8.5	1.58	1.89
1.399	14.604	0.047	20.4	17.8	3.74	3.76	8.5	1.53	1.85
1.433	14.750	0.018	5.6	4.8	3.41	3.42	8.9	1.40	1.51

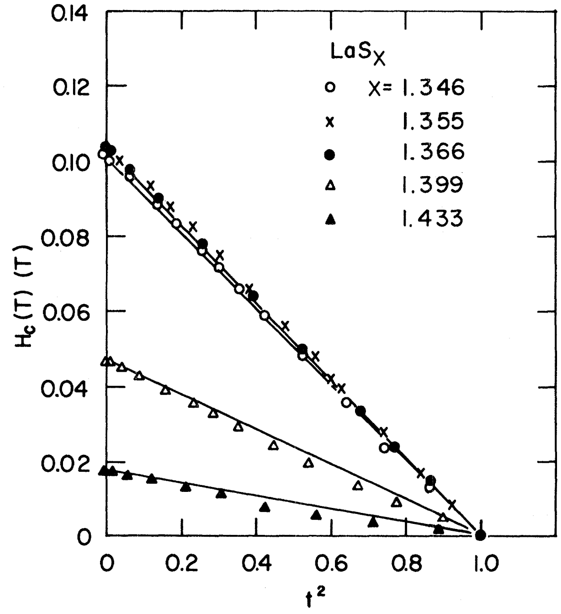

FIG. 9. Thermodynamic critical field $H_c(T)$ of LaS_x vs t^2, where $t=T/T_c$.

The jump in the heat capacity at T_c, ΔC, can be estimated by using the Rutgers' relation[24]

$$\Delta C(\text{calc})=\frac{VT_c}{4\pi}\left[\frac{dH_c(T)}{dT}\right]^2_{T=T_c} . \tag{8}$$

Table II also shows the calculated and observed values of ΔC for the five LaS_x specimens. According to Goodman,[25] the value of the energy gap at $T=0$ can be obtained from the relation

$$\frac{2\Delta(0)}{kT_c}(\text{calc})=\frac{4\pi}{\sqrt{3}}\left[\frac{H_c(0)^2V}{8\pi\gamma T_c^2}\right]^{1/2} , \tag{9}$$

where k is the Boltzmann constant. Using the values of $H_c(0)$, V, γ, and T_c given in Tables I and II, the energy gap for the five LaS_x specimens were calculated and they were found to be in good agreement (within 2%) with the "observed" values obtained from the $C_{es}/\gamma T_c$ data in Fig. 8. For a comparison with theory, it is convenient to plot the deviation function of critical field, $D(t)=H_c(T)/H_c(0)-(1-t^2)$, vs t^2. Figure 10 shows the analyzed results for LaS_x of $x=1.346$, 1.355, 1.366, and 1.399 with the theoretical curves for $2\Delta(0)/kT_c=3.53$, 4.30, and 4.70, which were obtained by assuming $\Delta(T)/\Delta^{\text{BCS}}(T)=\text{const.}$[22] The $D(t)$ data for $\text{LaS}_{1.346}$, $\text{LaS}_{1.355}$, and $\text{LaS}_{1.366}$ have a similar tendency, changing sign near $t^2=0.5$ or 0.7 and becomes negative at high t^2 values. On the other hand, the data for $\text{LaS}_{1.399}$ agree with the BCS curve in general,

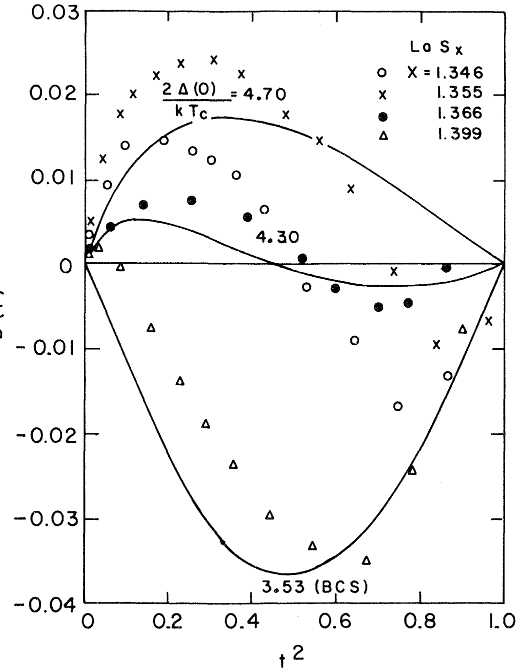

FIG. 10. Deviation function of thermodynamic critical field, $D(t) = H_c(t)/H_c(0) - (1-t^2)$, for LaS_x, where $t = T/T_c$. The solid curves are the results for the energy gap values of 3.53, 4.30, and 4.70, see Padamsee *et al.* (Ref. 22).

but take positive values below $t^2 = 0.08$. These results again suggest that these LaS_x alloys (for $x < 1.38$) are strong-coupling superconductors.

IV. DISCUSSION

A. Crystal chemistry and superconductivity

In this section the superconductivity of the LaS_x samples in relation to their crystal structure and bonding is discussed. Figure 11 summarizes the results of heat capacity and electrical resistivity measurements in the LaS_x compounds. As can be seen from this figure, an important feature of the heat-capacity data of LaS_x is that γ and Θ_D, respectively, increase and decrease as x becomes smaller and exhibit discontinuities near $x = 1.43$. The cubic to tetragonal transformation in $LaS_{1.346}$ and $LaS_{1.355}$ has no effect on the Θ_D in relation to the compositional variation of Θ_D, but causes a remarkable lowering of γ indicating a significant change in the Fermi surface and the density of states.

The Debye temperature is related to the compressibility K_c by the equation[26]

$$\Theta_D = A K_c^{-1/2} \mu^{-1/3} \rho^{-1/6} \ . \qquad (10)$$

Here, A is a constant for isostructural solids, μ the

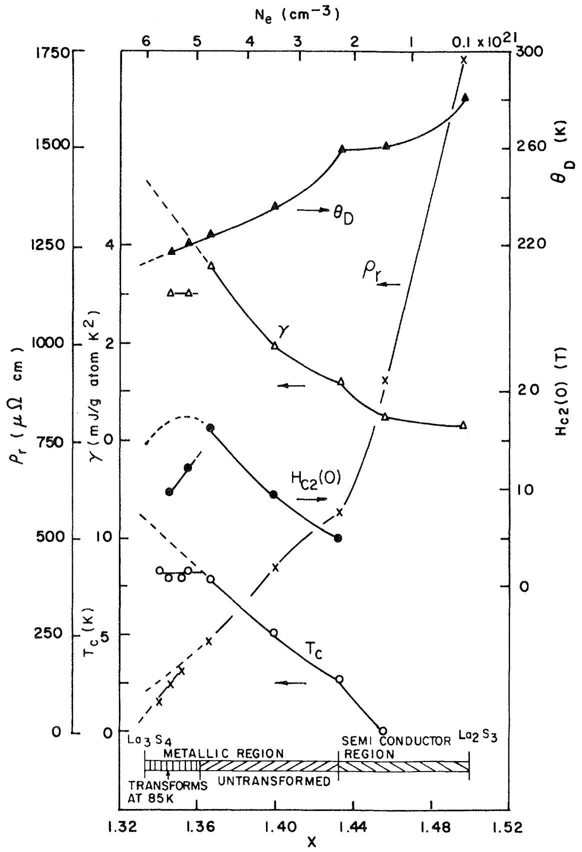

FIG. 11. Summary of the results of the heat capacity and electrical resistivity measurements for the LaS_x compounds. The resistivity values given are taken at 4.2 K or a temperature just above T_c^*. The dashed lines are the expected values if the cubic form did not transform to the tetragonal phase.

molecular weight and ρ the density of the substance under consideration. If we make a comparison between $LaS_{1.366}$ and $LaS_{1.496}$, where the crystallographic transition at low temperatures does not occur,[16] one finds $[\mu(1.366)/\mu(1.496)]^{-1/3} = 0.977$, $[\rho(1.366)/\rho(1.496)]^{-1/6} = 0.989$, and the product of these two terms $= 0.966$. But since $\Theta_D(1.366)/\Theta_D(1.496) = 0.794$, either the compressibility of the LaS_x compounds varies considerably with x or Eq. (10) does not hold. On the other hand, Θ_D is connected with the melting point T_m of the solid ($\Theta_D \propto T_m^{1/2}$).[26] According to the recent study of the La-S system,[27] T_m is $\sim 2130\,°C$ for $x = 1.333$ and $\sim 1960\,°C$ for $x = 1.500$. If the melting point were the dominant factor then the ratio $\Theta_D(1.366)/\Theta_D(1.496)$ should be > 1.0, and thus the drop in Θ_D observed as x decreases is even more remarkable, but is consistent with a lattice softening as x approaches 1.333. Assuming Eq. (10) is valid and by using the above ratios one finds that $K_c(1.366) = 1.48K_c(1.496)$, which is reasonable in view of the fact that alloys with $x < 1.362$ undergo a bcc to tetragonal low-temperature phase transformation. The LaS_x compounds are considered to be ionic crystals[28] and that the lanthanum and sulfur atoms have the usual valences of 3+ and 2−, respectively. With decreasing x, the concentration of the excess electrons (i.e., the conduction electrons) N_e increases. These excess electrons, which negatively contribute to the ionic bonding, may decrease the lattice energy U. Moreover, the electrical properties of LaS_x compounds change from semiconducting to metallic in the lanthanum-rich region beyond this composition (i.e., $x < 1.43$), according to the electrical resistivity measurements.[16] These facts seem to support our consideration about the composition dependence of Θ_D of LaS_x.

According to the BCS theory[21] of superconductivity, there is a relation between T_c, the average phonon energy $\hbar\langle\omega\rangle$ and the interaction strength $N(0)V_p$:

$$kT_c = 1.14\hbar\langle\omega\rangle \exp[-1/N(0)V_p] \quad . \tag{11}$$

Here, $\hbar = h/2\pi$ and h is the Planck's constant, $N(0)$ the electronic density of states at the Fermi surface, and V_p the pairing potential arising from the electron-phonon interaction. According to the free electron model, the electronic specific-heat parameter γ is proportional to $N(0)$, that is

$$\gamma = 2\pi^2k^2N(0)/3 \quad . \tag{12}$$

Assuming $\hbar\langle\omega\rangle = k\Theta_D$ and combining Eqs. (11) and (12) it has been found that $\ln(T_c/\Theta_D)$ is proportional to γ^{-1}. This has been shown to hold for many superconducting materials.[29] As can be seen from Fig. 12 the $\ln(T_c/\Theta_D)$ vs γ^{-1} plot is nearly linear for the LaS_x compounds which do not transform to the tetragonal phase at low temperatures. The $\mathrm{LaS}_{1.346}$ and $\mathrm{LaS}_{1.355}$ samples, which transform to the tetragonal form at 85 and 55 K, respectively, do not fit, as would be expected because of the phase transformation.

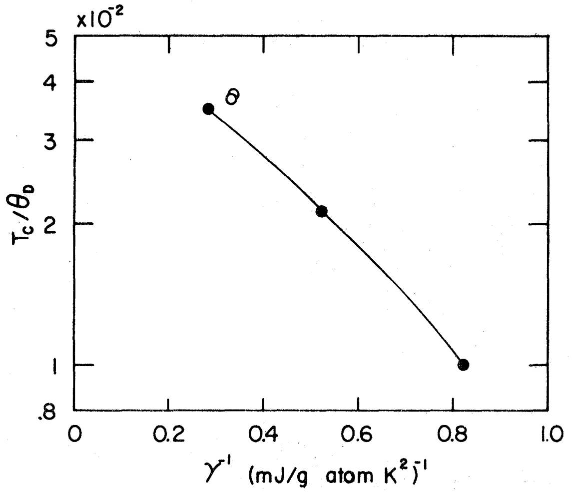

FIG. 12. Plot of $\ln(T_c/\Theta_D)$ against γ^{-1} for the superconducting LaS_x compounds. Open circles are for the $\mathrm{LaS}_{1.346}$ and $\mathrm{LaS}_{1.355}$ compounds which undergo a cubic to tetragonal transformation at 85 and 55 K, respectively. The solid circles are for $\mathrm{LaS}_{1.366}$, $\mathrm{LaS}_{1.399}$, and $\mathrm{LaS}_{1.433}$.

McMillan[30] explained theoretically that the transition temperature of strong-coupled superconductor is given by

$$T_c = \frac{\Theta_D}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.6\lambda)}\right] \quad , \tag{13}$$

where μ^* is the repulsive electron-electron interaction parameter (taken to be the same as that of lanthanum metal—0.08)[31] and λ the electron-phonon coupling parameter. Moreover, the electronic specific-heat parameter γ is enhanced by the factor $(1+\lambda)$ from the electron-phonon interaction. If λ and γ are known, we can calculate the electronic density of states at the Fermi surface $N(0)$ by using the following relationship:

$$N(0) = \frac{3\gamma}{2\pi^2k^2(1+\lambda)} \quad . \tag{14}$$

The values of λ and $N(0)$ calculated by using Eqs. (13) and (14) are given in Table I. The largest $N(0)$ value in the LaS_x specimens is 2.09 states/eV La atom for $x = 1.366$, which lies between the values for β-La (fcc) metal[32] (2.44 states/eV atom) and α-La (dhcp) metal[33] (2.00 states/eV atom).

B. Upper critical field and Ginzburg-Landau parameter

The C/T vs T^2 curves in $\mathrm{LaS}_{1.366}$ plotted in Fig. 4 show that the upper critical field at $T = 0$, $H_{c2}(0)$ is much larger than 10 T, suggesting that the LaS_x compounds are high critical field superconductors. From the theory of type-II superconductors as extended by Maki,[34] the parameters κ_1, κ_2, and κ are defined as

$$\kappa_1 = \frac{H_{c2}(T)}{\sqrt{2}H_c(T)} \quad , \tag{15}$$

$$\left[\frac{dM}{dH}\right]_{H=H_{c2}} = \frac{1}{4\pi\beta_A(2\kappa_2^2-1)} \quad , \tag{16}$$

$$(\beta_A = 1.18)$$

and

$$\kappa = \kappa_1(T_c) = \kappa_2(T_c) \quad . \tag{17}$$

Here, $(dM/dH)_{H=H_{c2}}$ is the slope of the magnetization curve at $H_{c2}(T_H)$. The values of $\kappa_1(T)$ calculated by using Eq. (15) are plotted in Fig. 13. The solid

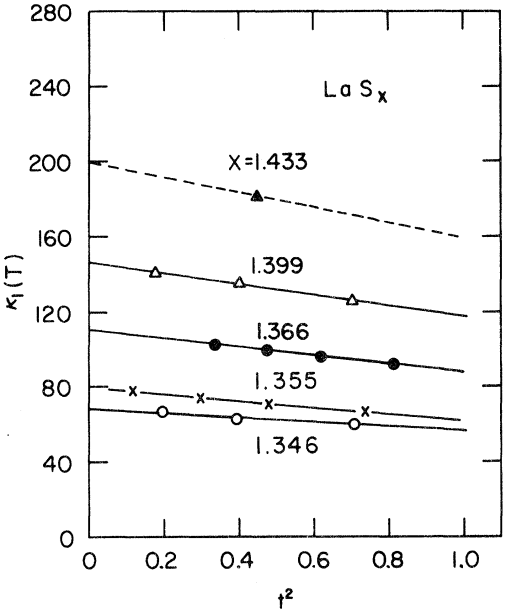

FIG. 13. Generalized Ginzburg-Landau parameter $\kappa_1(T)$ vs t^2, where $t=T/T_c$, for LaS_x. The solid lines are the results of least-squares fitting against $\kappa_1(T)=D_0-D_1t^2$. The slope for $LaS_{1.433}$ (dashed line) was estimated, see text.

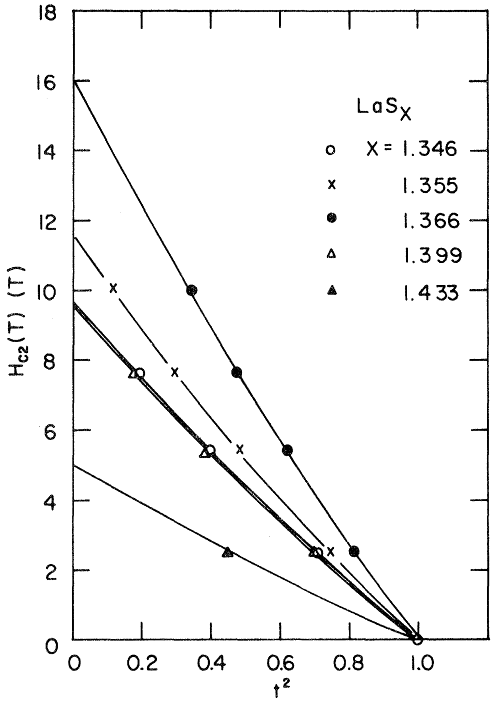

FIG. 14. Upper critical field $H_{c2}(T)$ of LaS_x vs t^2, where $t=T/T_c$. The solid lines are the results from Eq. (15) and the points are the experimental values.

lines in Fig. 13 are the results of least-square fitting of the data to the relationship $\kappa_1(T)=D_0-D_1t^2$, where D_0 and D_1 are fitting parameters. The temperature dependence of $\kappa_1(T)$ was theoretically discussed by Gor'kov[35] and by Helfand and Werthamer.[36] The analyzed results for $\kappa_1(T)$ of LaS_x, which are shown in Table III, give $\kappa_1(t=0)/\kappa=1.21$ to 1.31. These values of $\kappa_1(t=0)/\kappa$ in LaS_x are consistent with the results predicted by the above authors.[35,36] For $LaS_{1.433}$ the value of $\kappa_1(t=0)/\kappa=1.25$ was assumed in order to obtain the temperature dependence of $H_{c2}(T)$.

The upper critical fields $H_{c2}(T)$ for LaS_x were calculated from Eq. (15) by using the $H_c(0)$ values in Table II and the $\kappa_1(T)$ values in Table III. The $H_{c2}(T)$ curves of LaS_x compounds estimated in this way are shown in Fig. 14 along with the experimental results, the agreement is excellent. The upper critical field values at 0 K determined in this way are listed as $H_{c2}(0)$ (obs) in Table III. The maximum value, 16.2 T, was found for the $LaS_{1.366}$ composition confirming that the LaS_x compounds are hard type-II su-

TABLE III. The values of the electrical resistivity just above $T_c(\rho_r)$, the generalized Ginzburg-Landau parameters (κ_1, κ_2, and κ), and upper critical field at 0 K [$H_{c2}(0)$] for the superconducting LaS_x compounds.

			Ginzburg-Landau κ			
x	ρ_r ($\mu\Omega$ cm)	κ_1	From [$\kappa_1(t=1)$]	From [$\kappa_2(t=1)$]	$H_{c2}(0)$(obs) (T)	$H_{c2}(0)$(calc) (T)
1.346	121	$68.0-11.8t^2$	56.2	52.5	9.73	6.25
1.355	156	$79.1-18.8t^2$	60.2	57.0	11.67	8.32
1.366	232	$110.3-23.4t^2$	87.0	87.3	16.19	13.98
1.399	420	$145.8-28.8t^2$	117.0	115.4	9.67	8.60
1.433	565	$199.4-39.9t^2$	159.5	158.8	4.99	3.79

perconductors. It is also noted that the $H_{c2}(T)$ values for the tetragonal phase LaS$_x$ alloys ($x=1.346$ and 1.355) are smaller than the value for LaS$_{1.366}$, and that $H_{c2}(T)$ decreases with decreasing x when $x<1.366$. The composition dependence of $H_{c2}(0)$ (obs) in the LaS$_x$ compounds is shown in Fig. 11.

According to Kim *et al.*[37] the upper critical field in tesla at $T=0$ K for type-II superconductors can be expressed as

$$H_{c2}(0)=3.11\gamma\rho_r T_c \ , \tag{18}$$

where ρ_r is the normal-state resistivity in Ω cm and all other quantities are in cgs units. The upper critical field values at 0 K calculated by using Eq. (18) are shown as $H_{c2}(0)$ (calc) in Table III. For ρ_r we used the resistivity values at the temperature just above T_c^* from our electrical resistivity measurements of LaS$_x$.[16] As seen in Table III, the values of $H_{c2}(0)$ are too small in comparison with $H_{c2}(0)$ (obs), especially in LaS$_{1.346}$ where the superconducting peak in C/T vs T^2 curve (Fig. 2) is found even at 7.62 T. Indeed $H_{c2}(0)$ (calc) values obtained from Eq. (18) are in only fair agreement (~17%) with the observed data for the bcc alloys and in poor agreement (~47%) for the tetragonal alloys, see Fig. 15. The inclusion of strong-coupling effects in Eq. (18)[38] will account for an approximate 3% increase in $H_{c2}(0)$ (calc), which is still much smaller than $H_{c2}(0)$ (obs), especially for the tetragonal alloys. A more reasonable explanation for the discrepancies in the $H_{c2}(0)$ values is that the Fermi velocity is anisotropic.[39] Qualitatively one might expect the anisotropy of the Fermi velocity to be larger in the tetragonal alloys than in the cubic alloys and this would account for the larger difference between $H_{c2}(0)$ (obs) and $H_{c2}(0)$ (calc) for the tetragonal alloy.

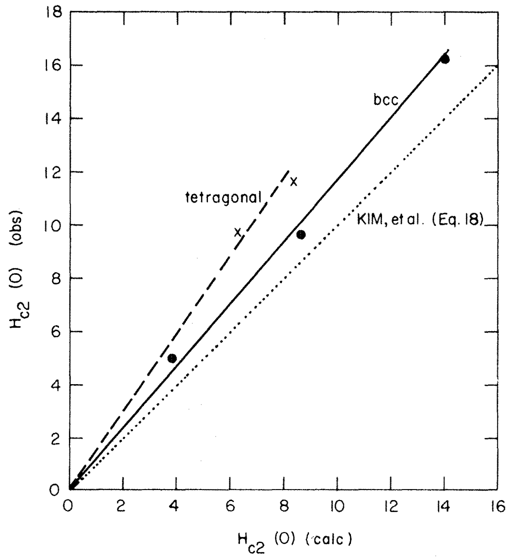

FIG. 15. Comparison of $H_{c2}(0)$ (obs) vs $H_{c2}(0)$ (calc). The data points would be expected to lie on the dotted line if Eq. (18) would hold for the LaS$_x$ alloys.

The $\kappa_2(T)$ values in the superconducting LaS$_x$ compounds were estimated as follows. According to Goodman,[40] the slope of the magnetization curve at $H_{c2}(T_H)$, $(dM/dH)_{H=H_{c2}}$, can be obtained from the relation

$$\frac{\Delta C}{VT_H}=\left(\frac{dM}{dH}\right)_{H=H_{c2}}\left(\frac{dH_{c2}}{dT}\right)_{T=T_H} \ . \tag{19}$$

From Eqs. (16) and (19), the values of $\kappa_2(T)$ were calculated by using the $H_{c2}(T)$ data and the observed ΔC and T_H values (Figs. 2–6). Figure 16 shows the temperature dependence of κ_2 values obtained in this way. The two values of the Ginzburg-Landau κ estimated from $\kappa_1(T)$ and from $\kappa_2(T)$ see Eq. (17), for each alloy are shown in Table III. Because the former value of κ was determined by extrapolating the best fit of the κ_1 value at the point $t^2=1$, while the latter value of κ comes directly from the ΔC data at T_c, the value of $\kappa=\kappa_2(t=1)$ is probably more reliable. However, the difference is only a few percent at the most (see Table III) for all alloys. As reported by Goodman,[41] the Ginzburg-Landau parameter κ can be expressed as

$$\kappa=\kappa_0+7530\gamma^{1/2}\rho_r \ , \tag{20}$$

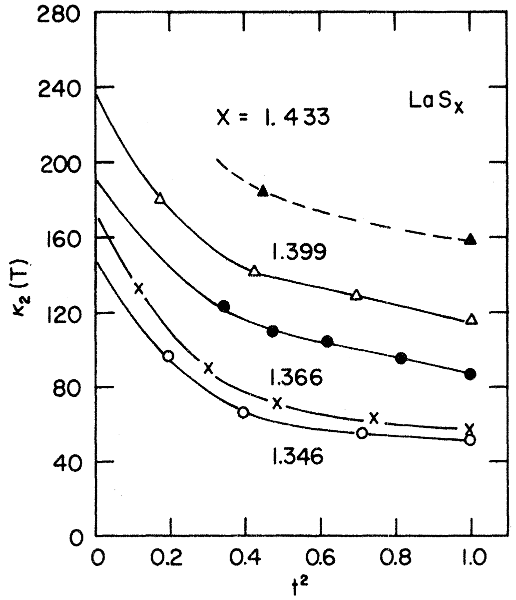

FIG. 16. Generalized Ginzburg-Landau parameter $\kappa_2(T)$ vs t^2, where $t=T/T_c$, for LaS$_x$. The solid lines are the results of least-square fitting of the equation $\kappa_2(T)=E_0+E_1t^2+E_2t^4+E_3t^6$.

TABLE IV. The intrinsic Ginzburg parameter (κ_0), the average Fermi velocity (V_F), the intrinsic coherence length (ξ_0), and the London penetration depth [$\lambda_L(0)$] for the superconducting LaS_x compounds, and also α-La.

x	κ_0	V_F (km/sec)	ξ_0 (Å)	$\lambda_L(0)$ (Å)
1.346	11.1	91	158	1830
1.355	3.9	158	262	1063
1.366	1.1	281	491	547
1.399	1.5	224	615	940
α-La[a]	2.35	133	363	888

[a] Reference 33.

where γ is in ergs/cm^{3}K^2 and ρ_r in Ω cm. The intrinsic Ginzburg-Landau parameter κ_0 for the superconducting LaS_x compounds was estimated from Eq. (20) by using the observed values of γ listed in Table I, the κ values from $\kappa_2(t=1)$ and ρ_r listed in Table III. The resultant κ_0 values are listed in Table IV. It is interesting that the κ_0 value of the $LaS_{1.346}$ specimen is ten times larger than the values in $LaS_{1.366}$ and $LaS_{1.399}$. This large difference may be connected with the fact that the former is the sample which undergoes the crystallographic transformation at low temperatures.[16]

These specific-heat data can be used to calculate several other superconducting and normal-state parameters. Gor'kov[35] showed that the parameter κ_0 may be written as

$$\kappa_0=\frac{0.96\lambda_L(0)}{\xi_0}\ , \tag{21}$$

and Hake[42] reported that the intrinsic coherence length ξ_0 and the London penetration depth $\lambda_L(0)$ can be determined from the relations

$$\xi_0=\frac{0.18kS}{12\pi\gamma T_c} \tag{22}$$

and

$$\lambda_L(0)=\frac{3h\pi^{1/2}\gamma^{1/2}}{ekS}\ , \tag{23}$$

where e is the electronic charge in emu and S is the area of the Fermi surface in $\vec{k}$ space, and all quantities are in cgs units. Substituting Eqs. (22) and (23) into Eq. (21), the parameter κ_0 can be expressed as

$$\kappa_0=1069\frac{h\gamma^{3/2}T_c}{ek^2S^2}\ . \tag{24}$$

As reported by Fawcett,[43] the average velocity V_F is given by

$$V_F=\frac{k^2S}{6h\gamma}\ . \tag{25}$$

By using the S values estimated from Eq. (24), one obtains the values of V_F, ξ_0, and $\lambda_L(0)$ for the superconducting LaS_x compounds which are given in Table IV. As can be seen from this table, the small intrinsic coherence lengths are for the samples which undergo the crystallographic transition. These values are about $\frac{1}{2}$ to $\frac{1}{4}$ of the values for $LaS_{1.366}$ and $LaS_{1.399}$, respectively. On the other hand, the London penetration depth $\lambda_L(0)$ for the former are significantly larger than the values for the latter. The small ξ_0 and large $\lambda_L(0)$ values of $LaS_{1.346}$ and $LaS_{1.355}$ result from the decrease of the average Fermi velocity V_F relative to $LaS_{1.366}$ and $LaS_{1.399}$. This decrease in V_F seems to be due to the change of the shape of Fermi surface produced by the cubic to tetragonal phase transition, which was earlier noted when discussing the decrease in γ for these alloys.

It is interesting to note that the corresponding values [κ_0, V_F, ξ_0, and $\lambda_L(0)$] for α-La (dhcp) fall between the two groups of LaS_x alloys, except for the London penetration depth.

C. Influence of the phase transformation on superconductivity

As noted above the superconducting transition temperature is nearly constant over the composition range $1.333 \leq x \leq 1.362$ (see Fig. 11); this was also verified by Westerholt.[11] Furthermore almost all of the reported T_c values for "La_3S_4"[2,8–11] are almost the same (8.2–8.3 K), notwithstanding the fact that it is difficult to get the perfectly stoichiometric La_3S_4 compound because the minimum vapor pressure of this system lies at a sulfur-rich composition of $x > 1.333$.[44] Furthermore, because the T_c of the cubic LaS_x phase has a strong compositional dependence between $x = 1.366$ and 1.500 the vapor pressure minimum probably lies between $x = 1.333$ and $x = 1.366$.

The constant T_c value in this region is probably related to the constant γ value observed for these alloys (Fig. 11). Apparently the increasing electron concentration on going from $x = 1.362$ to 1.333 has little or no effect on T_c, unlike what is observed for the concentration range $1.366 \leq x \leq 1.500$.

As the sulfur content decreases from $x = 1.500$ toward 1.333, a lattice instability sets in as exhibited by a low temperature (< 200 K) cubic to tetragonal transformation. The critical composition appears to be $x = 1.362$,[16] for $x < 1.362$ the cubic phase transforms. As the sulfur content decreases approaching the critical concentration, the T_c and H_{c2} values are rapidly rising (Fig. 11) reaching a maximum at the point where the lattice exhibits its maximum instability without undergoing a transformation. Beyond that point (lower sulfur contents), the T_c and H_{c2} values have degraded considerably when compared to the expected values if the cubic to tetragonal transformation did not occur (dashed lines in Fig. 11). For example, the respective expected values are 9.7 K and 17.0 T for $LaS_{1.346}$ which compare to the observed values of 8.0 K and 9.7 T, respectively. Here, the expected value from $x = 1.333$ to 1.366 for $H_{c2}(0)$ was estimated by using Eq. (18) [except a constant of 3.60 was used instead of 3.11 so that the $H_{c2}(0)$ (calc) value agrees with $H_{c2}(0)$ (obs) value for $LaS_{1.366}$] and the linearly extrapolated values of γ, ρ_r, and T_c.

These results are also consistent with the commonly held ideas that the superconductivity is more favorable for a phase with a cubic structure than one with lower symmetry (e.g., tetragonal). However, the fact that the electronic specific-heat parameter is also greatly diminished below that expected if the transformation did not occur (the expected value $= 4.2$ mJ/g at. K^2 versus the observed value $= 3.0$ mJ/g at. K^2 for $LaS_{1.346}$) probably accounts for a large part in the reduction of the $H_{c2}(0)$ value. The crystal structure plays an important role in determining the Brillouin zone of the solid and the symmetry of the ion core potentials seen by the conduction electrons, and thus strongly influences the γ values. But one cannot *a priori* state which structure would favor a high γ or a low γ, until a complete band-structure calculation has been performed for each particular structure. It would, however, appear that this structure transformation is electronically driven. That is, as the density of states increases as the sulfur content approaches the critical value ($x \cong 1.36$), the free energy can be lowered by redistributing the conduction electrons in the tetragonal phase, such that the density of states is also reduced. However, additional experiments, such as, UPS, XPS, inelastic neutron scattering, tunneling, etc., along with theoretical band-structure calculations would be useful in understanding the nature of the bcc-tetragonal transformation and its influence on superconductivity.

D. Comparison with other results

The recent results of Westerholt *et al.*[10,11,13] are in qualitative agreement with our results with respect to T_c, T_M (the bcc to tetragonal transformation), γ, Θ_D, and $H_{c2}(0)$. There is excellent agreement as to the magnitude of these values, especially the values near the La_3S_4 stoichiometry. But at higher sulfur contents there is some disagreement. Although the general trends are the same, there is a 1 to 2% difference in the alloy composition for the same value of the property, see Fig. 17.

We believe that this discrepancy can be explained by the presence of oxygen in the samples of Westerholt *et al.*[11] Their alloy compositions are nominal compositions, but since the alloys were prepared in sealed crucibles they should be accurate to about four significant figures. Our alloys were prepared in general in open crucibles, some sulfur was lost, and thus all of our samples after preparation were chemically analyzed to determine the composition, which should also be accurate to about four significant figures. Thus the procedure for determining the com-

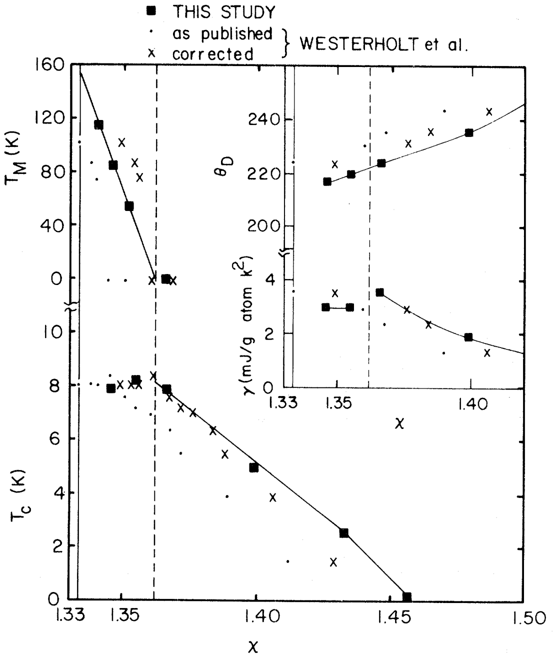

FIG. 17. Comparison of the superconducting transition temperatures, the cubic to tetragonal polymorphic phase transition temperatures, the electronic specific-heat constants and Debye temperatures obtained in this study and those reported by Westerholt *et al.* (Refs. 10, 11, and 13). The discrepancy between the values reported by Westerhold *et al.* and ours is thought to be due to oxygen impurities in their starting lanthanum metal, and correcting for this impurity shifted the values as indicated, see text for more details.

positions are equivalent and cannot account for the discrepancy. But since Westerhold and co-workers used commercial lanthanum metal, it is quite likely that their metal contained at least 1 at. % oxygen,[45] which is present as La_2O_3 in the lanthanum metal. But since La_2O_3 is much more stable than any LaS_x composition over the temperature range of 0 to 2500 K (e.g., ΔG_f^0 at 298 K is −407.9 kcal/mole for La_2O_3 and −303.7 kcal/mole for La_2S_3)[46,47] the La_2O_3 present in the alloy will not react to form LaS_x, especially in a closed system. Thus the authors have less available lanthanum metal than they thought to react with the sulfur, and their compositions are all richer in sulfur than is calculated from the weights of the two components. Assuming that 1 at. % oxygen is present in their starting lanthanum we have recalculated their compositions, which are shown as *x*'s in Fig. 17. It is seen that the agreement for their "corrected" values and our results is quite good, except for the high sulfur content alloys where the agreement is fair. As noted in Sec. II of this paper our lanthanum metal only contained 0.0295 at. % oxygen, and this small amount of oxygen has a negligible effect on our alloy compositions.

The agreement between our γ and Θ_D values and those of Westerhold and co-workers are quite good. Especially when one considers that Westerhold *et al.* used zero field heat-capacity data to extrapolate to $T=0$ to obtain γ and Θ_D, even though the temperature range from which the extrapolations were made were well above $\frac{1}{50}$ of Θ_D, which is usually considered the upper limit of the Debye T^3 law.

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