Resistivity Saturation in fcc La under High Pressure

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Data are presented for the electrical resistivity ρ of fcc La as a function of T and p in the range 70 to 700 K and 0 to 1.25 GPa. The data are analyzed using the phenomenological "parallel resistivity" formula for resistivity saturation, which describes very well the T dependences of both ρ and its pressure coefficient. The pressure coefficients of the electron-phonon interaction parameter and T_c are calculated from the p dependence of the electron-phonon component, and the p dependence of the parallel saturation resistivity is obtained from band-structure calculations using a simple Bloch-Boltzmann model. In both cases excellent agreement with experiment is found.

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Lanthanum metal is known to have a number of interesting and unusual properties. To name but two examples, it has an unusually high superconducting critical temperature T_c, and a very high electrical resistivity ρ, which tends to saturate towards a limiting value at high temperatures T. At and below room temperature, La exists in two allotropic forms [1], one with the fcc structure and one with a double hexagonal close-packed (dhcp) structure, and with T_c's of 6 and 5 K, respectively [2–4]. An approximate phase diagram, adapted from Ref. [1], is shown in Fig. 1. The fcc structure is basically a high-T, high-pressure phase, while the dhcp form is stable at low pressure p and below 525 K. In the hatched area both phases can be stabilized and the actual structure depends on past thermal history [1], and both phases can thus be studied at normal p below about 350 K. In both phases T_c increases extremely rapidly [2–4] with p, such that La has [2] the highest T_c known for any elemental solid, 13 K, above 20 GPa.

The cause of the rapid increase in T_c with p has been the subject of some debate, and in an attempt to resolve this question we have recently [5] measured the resistivity of La as a function of T and p in the range 165–300 K and 0–7 GPa, and in both the dhcp and the fcc phases. From the data we tried to extract the p dependence of the transport electron-phonon interaction parameter λ_{tr}, using a method known to be successful [6,7] with other (simple and transition) metals. For comparison we also presented [5] theoretical calculations of the band structure, Fermi surface properties, and λ_{tr} as functions of p. The differences between results for λ_{tr} obtained by different methods were surprisingly large in view of the very accurate results [6,7] found for $d\lambda_{tr}/dp$ for other metals by the same method. One surprising result, contributing a large part of the uncertainty in the final data, was that the pressure coefficient $d\ln R/dp (= R^{-1} dR/dp)$ of the resistance R varied strongly with T. For simple metals no significant T dependence is expected [8] (or observed) in $d\ln R/dp$ (or $d\ln\rho/dp$) above $\Theta_D/2$, where the Debye temperature Θ_D for La is [9] 150 K, but for both dhcp and fcc La $d\ln R/dp$ decreased from approximately zero near 175 K to between -0.01 and -0.02 GPa^{-1} at 300 K. Since the pressure coefficient of λ_{tr} is calculated from $d\ln\rho/dp$ [see Eq. (2) below], a similar variation with T was found for $d\ln\lambda_{tr}/dp$. Although the data for $\rho(p,T)$ near 295 K were in excellent agreement with both our own previous data [7] and with literature data [10], some doubts remained about the low-T results; however, a later study showed [11] that the increase in $d\ln R/dp$ with decreasing T persisted down to 70 K for fcc La.

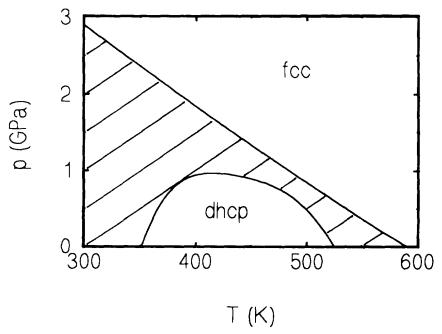

FIG. 1. Approximate phase diagram for La, adapted from Ref. [1]. In the hatched area, both phases are stable.

To further investigate this effect, measurements have now been carried out up to 700 K. The results show that $d\ln\rho/dp$ decreases over the whole range of T investigated, from 70 to 700 K. To our surprise, the results can be very well described by the phenomenological "resistivity saturation" model [12–14]. Not only can ρ vs T be described in terms of a constant resistivity ρ_p in parallel with the electron-phonon resistivity ρ_{ep}, but the model also describes (in fact, *predicts*) the T dependence of $d\ln\rho/dp$ over the whole range in T investigated, assuming constant but different values for the pressure coefficients of ρ_{ep} and ρ_p.

Two La specimens were cut from a wire, 1 mm in diameter and with a stated purity of 99.9%, obtained from Goodfellow Ltd., Cambridge, U.K. Thin wires were spot welded to the specimens to form a type-K thermocouple and four contacts for dc four-probe resistance measurements, using current reversal to eliminate thermal effects.

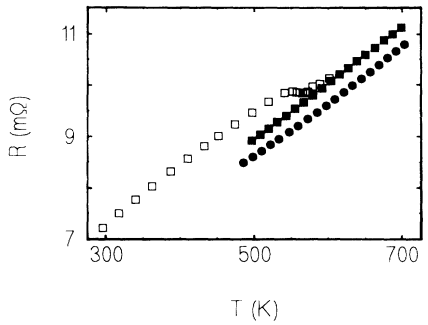

FIG. 2. Resistance vs increasing T for one specimen. □: 0.3 GPa, first run; ■: 0.3 GPa, second run; ●: 1.25 GPa.

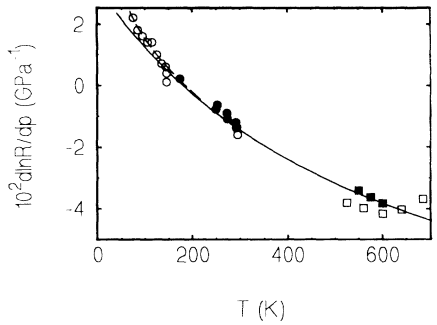

FIG. 3. Pressure coefficient of resistance, $d\ln R/dp$, vs T. ■: this work, sample 1; □: this work, sample 2; ●: Ref. [5]; ○: Ref. [11]. See text for definition of fitted curves.

The high-pressure vessel used was the same 70 mm in internal diameter piston-and-cylinder device as used in a previous study [15] on Ni. The internal oven [15] was modified to eliminate temperature gradients by taking the connection leads out through loose-fitting end plugs made from Al_2O_3 tubes, provided with heating coils. Manual adjustment of the power to these kept the temperature difference between oven center and ends below 0.2 K. The pressure medium used was dc 200 silicone oil and p was measured with a Manganin gauge. Contrary to literature reports [16], dc 200 was stable only to 700 K, pyrolyzing rapidly above. Since the gas released reacted with the sample no measurements could be carried out above 700 K.

Virtually identical results were obtained for the two specimens. Figure 2 shows R as a function of increasing T for one specimen, at 0.3 and at 1.25 GPa, and from 300 to 700 K. The initial structure at 300 K is probably mainly dhcp, and the dhcp to fcc transformation (see Fig. 1) is indicated by a drop in R above 550 K during the first temperature increase. To ensure complete transformation the samples were left at 600 K for at least 1 h before measurements were begun. R was then measured as a function of T between 500 and 700 K at 0.3, 0.6, 0.9, and 1.25 GPa. (Indicated pressures are approximate; increasing T from 500 to 700 K usually resulted in a pressure increase of 20 MPa.) Finally, both samples were cooled to 300 K at $p > 1$ GPa and brought back to zero pressure. The material remained in the fcc phase during the temperature decrease as predicted by the phase diagram in Fig. 1, but reverted to dhcp during the final pressure decrease, possibly because of cold work due to solidification of the pressure medium [17].

Figure 3 shows experimental data for $d\ln R/dp$ for fcc La between 70 and 700 K, both from this work and from Refs. [5,11]. The strong T dependence previously observed is clearly verified. Searching for a way to analyze these data in a consistent way, it was found that the phenomenological "resistivity saturation" model [12–14] worked surprisingly well. In this model a constant resistivity ρ_p is assumed to act in parallel with the standard electron-phonon term ρ_{ep}, and the total resistivity ρ can be written

$$\rho^{-1} = (\rho_{ep})^{-1} + (\rho_p)^{-1} . \tag{1}$$

Equation (1) is usually assumed to describe the fact that the mean free path of electrons is limited to a minimum value equal to the interatomic spacing, and resistivity saturation is almost universally observed as the mean free path approaches [18] 10 Å. Fitting Eq. (1) to the literature data [19,20] for ρ shown in Fig. 4 (excluding the data below Θ_D), gave $\rho_{ep} = 0.277T$ $\mu\Omega$ cm and $\rho_p = 173$ $\mu\Omega$ cm. The two components are assumed to have different, temperature-independent pressure coefficients $d\ln\rho_{ep}/dp$ and $d\ln\rho_p/dp$, and from Eq. (1) the pressure coefficient of the total ρ is easily shown to be

$$d\ln\rho/dp = \rho_p(\rho_{ep}+\rho_p)^{-1} d\ln\rho_{ep}/dp + \rho_{ep}(\rho_{ep}+\rho_p)^{-1} d\ln\rho_p/dp . \tag{1'}$$

A simple fitting procedure applied to the data for $d\ln\rho/dp$ at $T > \Theta_D$ gave the full curve shown in Fig. 3 and defined by the parameters $d\ln\rho_{ep}/dp = +0.018$ GPa^{-1} and $d\ln\rho_p/dp = -0.125$ GPa^{-1}. Using instead the data from Ref. [5] only, we find virtually identical values for both parameters, and in this sense Eqs. (1) and

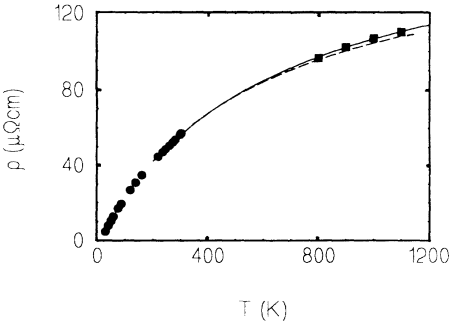

FIG. 4. Resistivity vs T for fcc La. ●: Ref. [19]; ■: Ref. [20]. The full curve has been fitted to the data using Eq. (1); dashed curve denotes resistivity data at constant volume.

(1') actually *predict* the data presented here and in Ref. [11]. Below Θ_D, Bloch-Grüneisen theory [8] predicts an increase in $|d\ln\rho_{ep}/dp|$ by a factor of 3 down to $T=0$, due to the shift from $\rho \propto T/\Theta_D^2$ at $T > \Theta_D$ to $\rho \propto T^5/\Theta_D^6$ as $T \to 0$. Adding this increase in $d\ln\rho_{ep}/dp$, scaled from Bloch-Grüneisen theory, to the total calculated $d\ln\rho/dp$ without changing the fitted parameters results in the dashed low-T extension of the curve, in even better agreement with the low-T data. Extrapolating the fitted function to higher T it is possible to calculate $\rho(T)$ for fcc La under constant volume (isochoric) conditions. The results of this calculation are shown as a dashed curve in Fig. 4; for La the correction is small, because of the small thermal expansivity [21] and the high compressibility [22] κ. Since theory usually assumes constant volume (or constant lattice parameters), such corrected data should always be used when comparing theoretical and experimental resistivity data.

For normal metals at high T, ρ can be written [23] $\rho=(8\pi^2 k_B/\hbar)T\lambda_{tr}/\omega_p^2$, where ω_p is the plasma frequency. The pressure coefficient is then $d\ln\rho/dp = d\ln\lambda_{tr}/dp - d\ln\omega_p^2/dp$, or [5-7]

$$d\ln\lambda_{tr}/dp = d\ln\rho/dp + d\ln\omega_p^2/dp \equiv d\ln\rho/dp + \kappa d\ln\omega_p^2/d\ln V . \quad (2)$$

In Eq. (2), ρ must be identified with the electron-phonon component ρ_{ep} discussed above. The volume dependence of ω_p^2, $q = d\ln\omega_p^2/d\ln V$, has been calculated [5] for fcc La with the (surprisingly large) result $q=2.5$, which inserted in Eq. (2) together with the experimental value for $d\ln\rho_{ep}/dp$ gives $d\ln\lambda_{tr}/dp = 0.12$ GPa^{-1}. This value may be compared with our previous estimates for the same quantity: Using Eq. (2) together with our data [5] for $\rho(p,T)$ between 170 and 300 K we found $d\ln\lambda_{tr}/dp = 0.025$ GPa^{-1}, while neglecting the T dependence of $d\ln\rho/dp$ and using only data from near 300 K resulted in $d\ln\lambda_{tr}/dp = 0.075$ GPa^{-1}. A theoretical calculation [5] gave an intermediate value of 0.05 GPa^{-1}. All these values are significantly lower than the present one. If we assume, as before [5-7], that $d\ln\lambda_{tr}/dp$ equals $d\ln\lambda/dp$, we can use McMillan's formula to calculate T_c vs p. In the calculation we use [9] $\Theta_D = 142$ K, with a p dependence given by the Grüneisen parameter [9] $\gamma_g = -d\ln\Theta_D/d\ln V = 0.7$. The value for μ^* was chosen as 0.13, independent of p as before [5,7]. Our previous calculations [5] gave a value of 1.64 for λ at $p=0$; here, λ was chosen as 1, since this gives a value for T_c closer to the experimental value, and also agrees well with other estimates (see Ref. [5]). Scaling the results to the observed [2-4] $T_c = 6$ K at $p=0$ (since the formula overestimates [23] T_c) gives $dT_c/dp = +1.4$ K/GPa, by chance identical to the experimental value [3].

A similar fit to data for dhcp La from Ref. [5] yields $d\ln\rho_p/dp = -0.073$ GPa^{-1} and $d\ln\rho_{ep}/dp = +0.01$ GPa^{-1}, which with [5] $q=1.2$ gives $d\ln\lambda_{tr}/dp = 0.06$ GPa^{-1}. Using the same parameters as above we find $dT_c/dp = +0.67$ K/GPa, significantly lower than the experimental values [2-4] +1.3 to +1.9 K/GPa. Our previous estimates for $d\ln\lambda_{tr}/dp$ ranged from +0.028 [from Eq. (2)] to −0.02 (theoretical calculation), again all lower than the present value. To explain the large dT_c/dp in dhcp La it is thus still necessary to include spin fluctuation [5] effects.

Although the experimental results for ρ_{ep} and T_c seem to justify the use of this phenomenological model, there is still little theoretical justification for the introduction of ρ_p. Can we, for example, explain its large p dependence? As a first approximation, ρ_p might be expected to scale simply with the mean free path, i.e., as the lattice parameter a. This would give $d\ln\rho_p/dp = \kappa/3 = +0.013$ GPa^{-1}, which does not agree with the present experiment. On the other hand, in a study of ρ vs p at 295 K for high-resistivity amorphous and crystalline transition-metal alloys, Cote and Meisel [24] found that $d\ln\rho/dp$ always approached zero as ρ increased above 80 $\mu\Omega$ cm. However, in their experiment the high resistivities were mainly due to high impurity or disorder resistivities, which might have a different p dependence than a saturated electron-phonon resistivity. In a more realistic theory for ρ_p, the p dependence of the electron band structure must be taken into account. One simple application of generalized Bloch-Grüneisen theory assumes [14] that ρ_p equals the standard high-T limit for ρ_{ep}, but with a relaxation time τ given by $\tau = a/\langle v_F^2\rangle^{1/2}$, i.e., $\rho_p = (4\pi/\omega_p^2)\tau^{-1} = (4\pi/\omega_p^2)\langle v_F^2\rangle^{1/2} a^{-1}$, where v_F is the Fermi velocity. The pressure coefficient is then

$$d\ln\rho_p/dp = -d\ln\omega_p^2/dp + d\ln\langle v_F^2\rangle^{1/2}/dp + \kappa/3 = \kappa(\tfrac{1}{3} - q + d\ln\langle v_F^2\rangle^{1/2}/d\ln V) . \quad (3)$$

Inserting the calculated values [5] $d\ln\langle v_F^2\rangle^{1/2}/d\ln V = -1.25$ and $q=2.5$ for fcc La we find $d\ln\rho_p/dp = -0.135$ GPa^{-1}, in excellent agreement with the experimental value given above. For dhcp La the corresponding value is $d\ln\rho_p/dp = -0.107$ GPa^{-1}, again in good agreement with the experimental data.

The mechanism for resistivity saturation is still not understood [12,13], and it is quite surprising that the very simple ideas used above are able to give such an accurate quantitative description of the experimental data. However, it has been noted before [12-14,18] that the simple Boltzmann-Bloch-Grüneisen model gives surprisingly correct estimates for the saturation resistivity, although no good explanation for this has yet been found. The very good agreement with experiment observed here might be a coincidence, or particular to La, but the results suggest that further high-p, high-T studies might help to resolve the many open questions in this area.

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