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Resistivity, bandstructure and superconductivity of DHCP and FCC La under pressure

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Abstract. Electronic and superconducting properties of DHCP and FCC La are studied both by measurements of the electrical resistance as a function of temperature and pressure and by calculations of the band structure, Fermi surface properties and the electron–phonon interaction λ. The importance of a hydrostatic environment for reliable resistance measurements is stressed. The transport properties of both phases are similar with small and negative values of the pressure coefficient of resistance. In contrast, the band structure calculations show large differences between the two phases, particularly in the pressure dependence, e.g. of the density of states (DOS) and the plasma frequency. Two new remarkable properties of La have been found, adding to previously known anomalies. One is a strong temperature dependence of the pressure coefficient of resistance which decreases with increasing temperature in both phases. The other is a strong pressure dependence of the plasma frequency in the FCC phase, which is larger than in any other element known to us. From these results the pressure dependence of λ is obtained by two independent methods for each phase. For FCC, both methods give $\mathrm{d}\ln\lambda/\mathrm{d}p = 0.05 \pm 0.02\ \mathrm{GPa}^{-1}$, while for DHCP, a decrease of λ with pressure or an almost pressure independent λ is suggested. These results cannot fully explain the observed $T_c(p)$ in the FCC phase and fail completely in the DHCP phase. The contribution from spin fluctuations is calculated approximately and found to account qualitatively for this discrepancy. In particular, the DOS decreases slowly with pressure in the FCC phase which gives some decrease of the spin fluctuation contribution in this phase, while in the DHCP phase the DOS decreases strongly, leading to suppression of the spin fluctuations under pressure.

1. Introduction

Lanthanum possesses a number of interesting properties. For instance, at low temperatures and pressure the stable phase is DHCP but an FCC phase can easily be retained by quenching from high temperatures. Both of these phases are superconducting with T_c about 5 K for the DHCP phase and 6 K for the FCC phase and an unusually strong increase of T_c with pressure in both phases (e.g. Smith 1972). In the FCC phase at 20 GPa, T_c reaches 13 K (Balster and Wittig 1975), which is the highest value known for an elemental superconductor. Other outstanding properties of La are the low melting temperature, an anomalous negative thermal expansion at low temperatures (Andres

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1968), and an unusually strong temperature dependence of the magnetic susceptibility (Lock 1957), and the Knight shift (Blumberg *et al* 1960).

The question how these properties should be understood has been controversial. Early attempts focused on the role of the 4f level, with different contrasting theories as to whether this level rises or sinks with pressure and which of these situations favours superconductivity. Electronic band-structure calculations, on the other hand, suggest that the 4f level is of minor importance with only a small fraction of electrons at ambient pressure and a weak pressure dependence of this occupancy (Pickett *et al* 1980). Alternative explanations for the superconducting properties include an increased electronic stiffness η with increased pressure (Glocker and Fritsche 1978, Pickett *et al* 1980), a decrease under pressure of the Coulomb pseudopotential μ^* (Baquero and Lopez-Olazagasti 1984), and phonon properties such as softening (Wühl *et al* 1973) or an unusually strong pressure dependence of the average Grüneisen constant (Asokamani *et al* 1986). The recent discovery of a dip in the transverse [111] phonon branch of FCC La by neutron scattering (Stassis *et al* 1985) and the subsequent observation of such a dip in a pseudopotential band structure calculation (Wang *et al* 1986) have further emphasised the importance of phonon softening in our understanding of La.

The main motivation for the present experimental and theoretical work is to deduce pressure variations of λ in order to establish a consistent explanation of the T_c variation with pressure. In conventional band-structure calculations of λ in La, phonon softening is generally not included (Pickett *et al* 1980, Dakshinamoorthy and Iayakutti 1983). An alternative is to deduce $\lambda(p)$ from a combination of resistivity measurements and a calculation of the plasma frequency. The problem of phonon softening is then circumvented since the electron–phonon matrix elements are essentially measured by the resistance. This method has been successfully applied to a number of elements (Sundqvist *et al* 1985). For La, however, we find unusual complications from a strong temperature dependence of the pressure coefficient of resistance which introduces some uncertainty in these results.

To obtain complementary information we therefore use both of these methods and present results for the pressure and temperature dependence of the electrical resistance and band structure calculations for a series of reduced lattice parameters. These results also allow for an estimation of the variation of T_c with pressure and, as will be shown, a rather consistent picture emerges when spin-fluctuations are taken into account.

Some of these results were presented in a preliminary report (Jarlborg *et al* 1987). The plan of the present paper is as follows: the experimental technique and results are described in § 2. In § 3 the calculations are described and results are given for several average Fermi surface properties, the electron–phonon interaction and the spin fluctuation contribution. In § 4, we analyse the pressure dependence of T_c in view of these results. Section 5 summarises the main results.

2. Experimental techniques and results

2.1. The samples

Lanthanum wire of nominal purity 99.95 wt% was acquired from Koch Light Ltd. The residual resistance ratio was found to be 35. As received this sample was predominantly in the DHCP phase as revealed by a T_c of 5.05 K, intermediate between the literature values 4.9 K (Maple *et al* 1969) and 5.2 K (Smith and Gardner 1966). To obtain the FCC

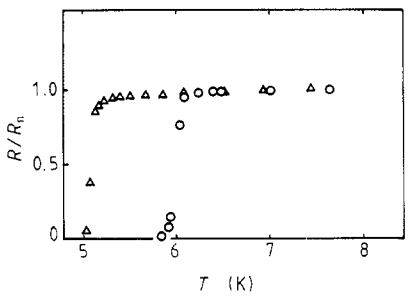

Figure 1. Resistive superconducting transitions for La: △, DHCP (as received); ○, FCC (after annealing at 370 °C for 3 h). R_n denotes the normal state resistance for each sample.

phase, part of the sample was cold-rolled and annealed at 370 °C for 3 hours and quenched by dropping the quartz ampoules in water. T_c was now 6.0 K. The superconducting transitions are shown in figure 1. After storing in vacuum for a long time this treatment was repeated prior to the measurements to ensure that no phase transformation had occurred.

The contact problems encountered earlier (Rapp and Sundqvist 1981) were now solved by spot welding thin Ni wires under a light mineral oil. Each contact was further strengthened by a drop of epoxy to preclude damage during assembly.

2.2. *Experimental equipment*

The electrical resistance was measured in a conventional four probe arrangement with a resolution of a few times 10^{-4}. The temperature T was measured using a chromel–alumel thermocouple, the calibration of which was assumed to be independent of pressure (Bundy 1961). The pressure p was measured *in situ* using a Manganin gauge (Sundqvist 1987).

The high pressure equipment used below 1.3 GPa was the same as described previously (Sundqvist and Rapp 1979) and we used freon cooling down to 250 K as before. To obtain lower temperatures we simply poured liquid nitrogen over the vessel. The temperature stability was then rather poor with variations up to 3–4 K. The pressure-transmitting medium used was a 50/50 mixture of n- and iso-pentane below 300 K and a silicone oil above 300 K. Both media are inert, do not dissolve significant amounts of water and are hydrostatic under these conditions of p and T (Sandberg and Sundqvist 1983, Sundqvist 1987).

To obtain pressures above 1.3 GPa, we have used a steel Bridgman anvil-type device capable of reaching 8 GPa (Andersson *et al* 1984, 1989). The same experimental technique was used except that the Manganin gauge was now calibrated *in situ* against the transition pressures of Bi. These measurements were made at 293 K only. As discussed by Andersson *et al* (1989), truly hydrostatic conditions are extremely important if accurate resistance data are to be obtained. In the present experiments, a 50/50 mixture of n- and iso-pentane was used as pressure transmitting medium, since it does not solidify until above 5 GPa. (Nomura *et al* 1982). In solid media large pressure gradients may arise causing internal strains in the samples and thus smearing the true $R(p)$. Comparatively soft solid media such as AgCl, or talc are widely used with Bridgman anvils (Bridgman 1952, Balster and Wittig 1975, Vijayakumar 1985), but it was noted already by Bridgman (1952) that in such media no accurate resistivity data can be obtained below some critical pressure p_c, which may be >3 GPa. In the case of La there is the further complication that DHCP La is transformed into the FCC phase if subjected

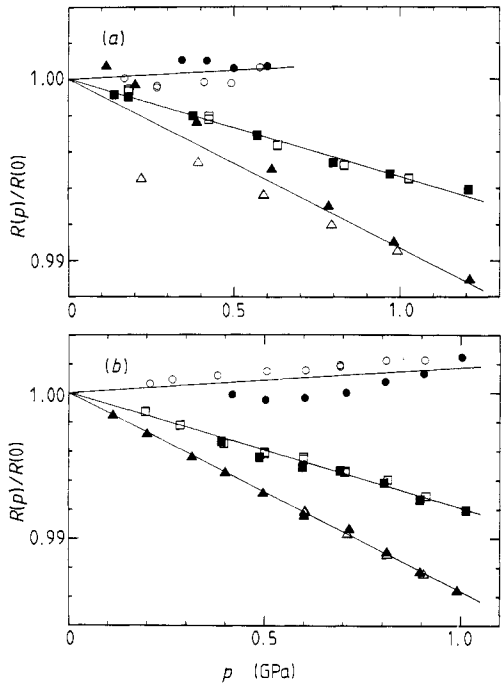

Figure 2. Relative electrical resistance $R(p)/R(0)$ as a function of pressure; full symbols indicate increasing pressure, open symbols decreasing p. (*a*) DHCP La: circles, 165 K; squares, 250 K; triangles 294 K. (*b*) FCC La: circles, 173 K; squares, 250 K; triangles, 294 K.

to deformation or cold-work (Balster and Wittig 1975), implying that the properties of the DHCP phase can only be studied under truly hydrostatic pressure.

2.3. Results in the low-pressure region

The use of two different pressure vessels and the existence of the DHCP→FCC phase transition at high p makes a subdivision of the results into two ranges, below and above 1.3 GPa natural.

At low pressures, the DHCP and FCC phases were studied in the temperature range 170–300 K. The temperature coefficient of resistivity at atmospheric pressure and 273.15 K was found to be $2.21 \times 10^{-3}\,K^{-1}$ and $2.40 \times 10^{-3}\,K^{-1}$ respectively for two DHCP samples, and $2.26 \times 10^{-3}\,K^{-1}$ for a FCC sample. These values are in fair agreement with previous results (Bridgman 1952, Legvold *et al* 1977, Rapp and Sundqvist 1981).

The resistance was measured versus pressure at several temperatures. It was not always possible to maintain the temperature quite constant, and small fluctuations (<1 K) could occur. In order to display the data graphically they were reduced for each pressure cycle to a constant (average) temperature. The resulting pressure dependence of R is shown in figure 2 for one DHCP and one FCC sample. The larger scatter at low T is likely due to the poor temperature control at these temperatures. In some pressure cycles an appreciable hysteresis (<0.25%) and non-linearity was observed. Similar behaviour has been observed previously (Bridgman 1951, 1952) and may be due to a slow phase transition in samples containing minor amounts of a second phase. For both phases at all temperatures R was found to vary linearly with p below 1.3 GPa.

It is clear from figure 2 that the pressure coefficient of resistance, B', depends on T. This was also noted previously in measurements of DHCP La over a smaller range of T and p (Rapp and Sundqvist 1981). In particular B' is found to be small and positive at

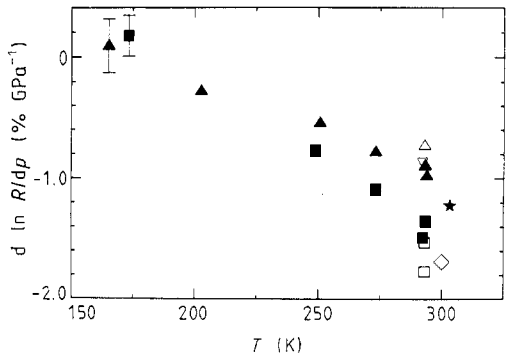

Figure 3. Pressure coefficient, $\mathrm{d}\ln R/\mathrm{d}p$, as a function of T. Full symbols denote low-pressure results; open symbols data obtained from the low-pressure part of a high-pressure (>2 GPa) investigation. △ and ▲, present results for DHCP La; □ and ■, present results for FCC La. ★, Bridgman (1927) (unknown structure); ◊, Bridgman (1952) (probably FCC); ▽, Nikolaev and Khvostantsev (1987) (DHCP).

the lowest temperatures and to decrease with increasing temperature, with negative values above 200 K in both phases. The results for B' are shown in figure 3; we show the results from all experiments where reasonable results were obtained. The estimated error in B' was usually of the same order of magnitude as the size of the symbol. In some low-T experiments larger uncertainties were found due to hysteresis and/or non-linearity. As an example, statistical errors are shown in the figure for the experiments at 160–170 K.

The pressure coefficient of resistivity β is obtained from B' as

$$\beta = \rho^{-1}\,\mathrm{d}\rho/\mathrm{d}p = B' - \tfrac{1}{3}\kappa \tag{1}$$

with the compressibility $\kappa = 4.06 \times 10^{-2}\,\mathrm{GPa}^{-1}$ from Vaidya and Kennedy (1970). β is negative at all temperatures and varies between $-1.1 \times 10^{-2}\,\mathrm{GPa}^{-1}$ at 175 K and $-2.6 \times 10^{-2}\,\mathrm{GPa}^{-1}$ at 300 K. The results will be further discussed in § 4.1.2 below.

There are several previous studies of $R(p)$ below 1.3 GPa in La. Our data for B' agree well with the early result by Bridgman (1927) shown in figure 3. Later Bridgman (1951, 1952) studied La of lower purity and of unknown crystal structure, and always found negative values of B'. In more recent studies positive values have been found (Balster and Wittig 1975, Vijayakumar 1985, Vijayakumar *et al* 1986a, b), but in these experiments solid pressure transmitting media have always been used, and such media are a source of large errors at low p. It is therefore gratifying to note that the recent data of Nikolaev and Khvostantsev (1987), obtained under truly hydrostatic conditions, are in excellent agreement with our results. We conclude that the pressure coefficients B' and β are small and negative in both low pressure phases of La in contrast to a recent calculation of $\rho(p)$, which predicts $\beta > 0$ (Iyakutti and Dakshinamoorthy 1986).

2.4. The high-pressure range ($p > 1.3$ GPa) and the DHCP–FCC transition

Two FCC samples were studied, with virtually indistinguishable results. The results from one of these experiments is shown in figure 4(*a*). For the DHCP phase the experiments on samples with the higher temperature coefficient of resistance failed and data could be successfully obtained only on parts of a sample which was crushed into pieces in an earlier experiment (Rapp and Sundqvist 1981). Part of this sample may therefore initially have been in the FCC phase. Although possibly a result of a moving potential contact, the sudden step in R at 0.7 GPa (figure 4(*b*)) may thus correspond to a transition to the stable DHCP phase and we have chosen to normalise the data to a value of $R(p = 0)$ obtained by extrapolating the data for $p > 1$ GPa. A small, similar step was observed

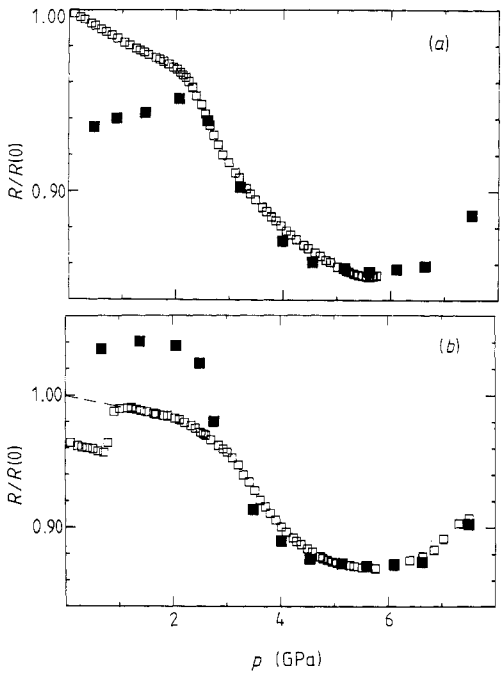

Figure 4. Relative electrical resistance versus pressure for (*a*) FCC La and (*b*) DHCP La. Open symbols, our data; full symbols, after Balster and Wittig (1975). The latter data have been normalised to ours at 5 GPa.

for the other DHCP sample at the same p. For one of the FCC samples we also noted a sudden increase in R by about 2% at 1.7 GPa, after which R continued to decrease above 2 GPa as in figure 4(*a*). Part of the metastable FCC phase might thus revert to the DHCP phase near the phase boundary.

The low-pressure part of the $R(p)$ curves can be compared with the results from the piston-and-cylinder experiment in § 2.3. The values of B' found for $p < 1.8$ GPa for the FCC samples and for $0.8 < p < 1.8$ GPa for DHCP samples are shown by open symbols in figure 3. While the results for B' for the FCC samples are somewhat smaller than the corresponding data from the piston-and-cylinder vessel, there is good agreement for the DHCP samples.

It is clear from figure 4 that R decreases monotonically with increasing p in both phases up to above 5 GPa. We also note that $\mathrm{d}R/\mathrm{d}p$ decreases fairly suddenly in *both* phases at about 2 GPa, while for the DHCP sample there is a further decrease in $\mathrm{d}R/\mathrm{d}p$ at 3.0 GPa. This latter anomaly probably corresponds to the DHCP → FCC transition, which in a recent study was found to start near 2.9 GPa at 293 K (Merkau and Holzapfel 1986). The former anomaly, present in both samples, probably corresponds to the isostructural electronic transition at about 2 GPa (Pickett *et al* 1980, Vijayakumar 1985). Under non-hydrostatic conditions it is usually not possible to resolve the two transitions by resistance studies. The slow increase in R above 6.5 GPa, saturating above 8 GPa (Balster and Wittig 1975, Nikolaev and Khvostantsev 1987) indicates the isostructural FCC–FCC transition (Balster and Wittig 1975, Wang *et al* 1986). It is possible that there is actually a sharp rise in R at the transition but that it is smeared by the non-hydrostatic pressure in this region.

In addition to our data we show in figure 4 data from Balster and Wittig (1975), normalised to our data at 5 GPa to show the good agreement between the two sets of data above 3 GPa. The difference in slope at low-p results from their use of a solid

medium. The data of Nikolaev and Khvostantsev (1987) agree well with our data below 2 GPa but their DHCP–FCC transition occurs at lower indicated pressure than for us, and the resistance anomaly is larger and has a larger slope than ours. The high-p isostructural transition also occurs at a higher pressure. The three sets of data show the same general trend, however, and the differences observed may be explained by differences in sample purity and heat treatment.

3. Calculations

3.1. Methods

The calculations were made using a self-consistent LMTO method using s, p, d, and f bases. Relativistic effects are included except for the spin–orbit interaction of the valence electrons. Other details of our LMTO calculations have been given previously (Jarlborg and Arbman 1977, Jarlborg *et al* 1983).

The FCC calculations were made in 505 k-points of the irreducible Brillouin zone while for the DHCP structure with 4 atoms per cell, the calculations were made using 144 k-points. The c/a ratio for DHCP La was chosen from experiments to be 3.225 and was fixed for all lattice constants chosen. The FCC and DHCP calculations were performed for ten different lattice constants chosen in such a way that the Wigner–Seitz radii remain always equal in the two structures. The density of states, Fermi velocity and plasma frequency have been calculated using a tetrahedron method from the LMTO k-points but not taking band crossings into account.

The influence of spin fluctuations has been calculated from the q-dependent Stoner factors (Jarlborg 1986). By applying staggered magnetic fields H with different wavelengths (or q), one can define the local Stoner enhancement $S = \xi/H$, where ξ is a measure of the response field. The relation to the local (on site) Stoner factor $\bar{S}$ is given by $S = 1/(1 - \bar{S})$. Here we have calculated S for two q-values: [000] and [100] in units of $2\pi/a$ for FCC La at the largest lattice constant. For all other cases (DHCP and other lattice constants), we scale the $\bar{S}(q)$-values by the total density of states at E_F, $N(E_F)$, since for one dominating band we usually have $\bar{S} = N(E_F)I$. This means that we neglect the pressure and structure variation of the exchange correlation integral I. In most cases I decreases slowly with applied pressure which indicates that our estimate of the decrease of S with pressure is not overestimated.

The total spin contribution to the apparent mass enhancement, λ_{sf}, is given by $0.5 \cdot \Sigma S_q \bar{S}_q^2$, where the sum is over the two spin waves. The calculated S and $\bar{S}$ are 2.38 and 0.58 for $q = 0$ and 1.37 and 0.27 for $q = [100]$. This shows that short wavelengths are more attenuated. The value of λ_{sf} is 0.14 for the FCC phase, corresponding to an average $\bar{S}$ of 0.41. This estimate of λ_{sf} is very approximate since only a few q are involved, but it does not contain any uncontrolled parameters.

The electron–phonon coupling λ has been calculated using the rigid-ion approximation. Such calculations combined with the McMillan (1968) equation for T_c are useful for a qualitative understanding of superconductivity (Papaconstantopoulos *et al* 1977) when spin-fluctuations are unimportant (Pictet *et al* 1987). The phonon part, $\langle\omega_{ph}^2\rangle$, is usually expressed as $0.5\,\theta^2$ where θ is the Debye temperature.

3.2. Band structure results

The band structure is shown along symmetry directions for two lattice constants of FCC La in figure 5 and of DHCP La in figure 6. The radii of the Wigner–Seitz spheres correspond

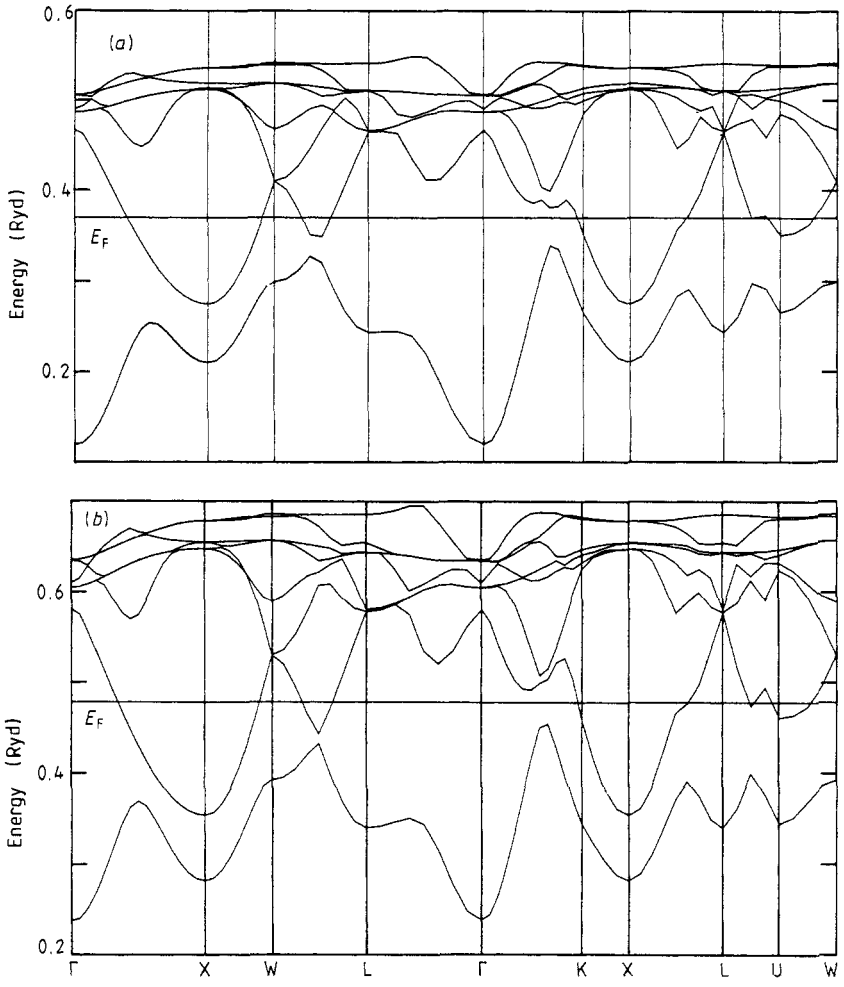

Figure 5. Band structure for FCC La: (*a*) at ambient pressure, (*b*) at 14% volume reduction corresponding to about 5 GPa. The Fermi level is shown by the horizontal line.

to ambient pressure and 14% volume compression, or a pressure of about 5 GPa, respectively.

In the FCC structure at ambient pressure the *f* bands are about 2 eV above E_F and are easily distinguished in the figure by their small dispersion throughout the zone. They are twined with the *d*-like bands in several regions of the zone while the only occupied band at the zone centre Γ is of s-character. At reduced volume the f bands rise relative to the Fermi surface and broaden considerably, while the d-like band second from the bottom of the figure, sinks relative to E_F, suggesting an increase in d-band occupancy with pressure.

The density of states (DOS) as a function of energy is shown at ambient pressure for both phases in figure 7. The scale has been chosen to display structure from the 4f states with their large DOS above the Fermi surface. The Fermi surface is situated in a region of relatively high DOS for both phases. A significant difference is that for FCC, E_F lies in the middle of such a region while for the DHCP phase, E_F is at the edge of a DOS peak.

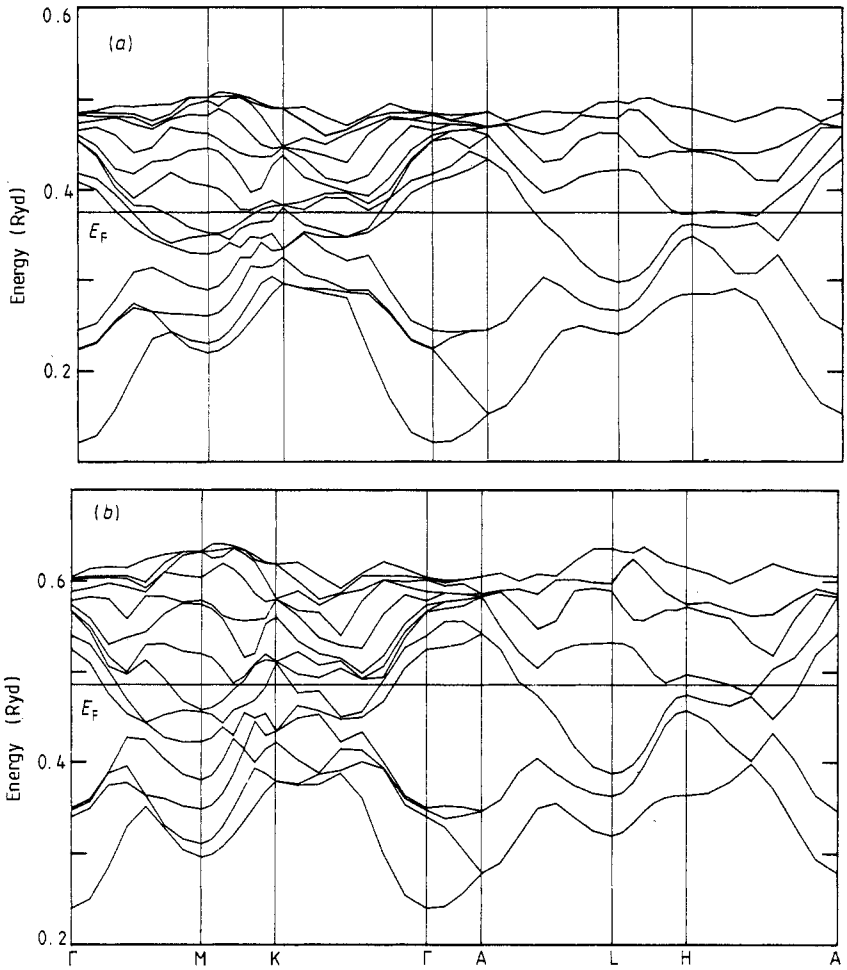

Figure 6. Band structure for DHCP La as in figure 5: (*a*) ambient pressure, (*b*) at 14% volume reduction.

From this observation a larger sensitivity can be anticipated for the pressure dependence of DOS-related properties in the DHCP phase compared to the FCC phase, as borne out by the results discussed in the next section.

Previous results for FCC La showing details of the band structure under pressure have been published by Glötzel and Fritsche (1977) in a non-self-consistent, semirelativistic rigorous-cellular-method and by Pickett *et al* (1980) in a fully relativistic, linearised augmented-plane-wave method. The overall agreement is quite good with both of these reports both regarding the band structure as well as the pressure dependence. In detail there are significant differences. As an example, consider the f bands at point X and ambient pressure: from Glötzel and Fritsche one finds that the centre of the bands is located 200 mRyd above the Fermi energy with a band width of 30 mRyd. The corresponding values from Pickett *et al* are 167 and 37 mRyd while we find 150 and 25 mRyd. Under pressure Pickett *et al* find 191 and 39 mRyd at 5 GPa and 208 and 44 at 12 GPa. Our results are 184 and 31 mRyd at 5 GPa while Glötzel and Fritsche obtain about 280 and 44 mRyd at 12 GPa.

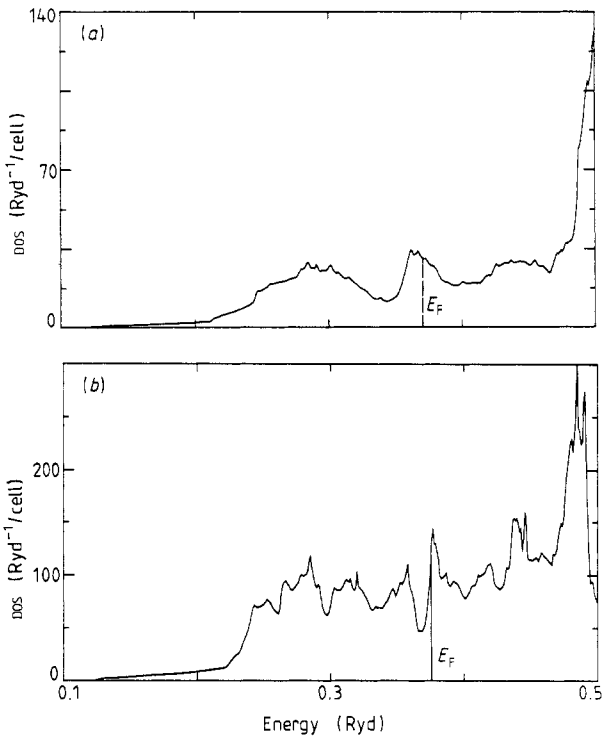

Figure 7. Density of states for La at ambient pressure: (*a*) FCC, (*b*) DHCP. E_F is shown by vertical lines.

For the DHCP phase it appears that band-structure calculations have not previously been published. The band structure and density of states are shown in figures 6 and 7. Since DHCP has 4 atoms per cell more bands appear in the corresponding Brillouin zone (BZ) compared to the FCC case. The picture shows some 'wiggles' due to the neglect of band crossings as seen along MK. Some bands have large dispersion and large v_F along ΓM, ΓK, LA and HA. (Note that BZ distances are smaller than for the FCC BZ.) A flat band is situated near E_F around the HK region and gives a peak in the DOS. At higher pressure this band moves upward relative to E_F and becomes more dispersive. As a result $N(E_F)$ decreases rapidly with pressure, since E_F moves to the left away from the peak. Compared to FCC, this implies a more delicate situation for $N(E_F)$-dependent quantities. The angular momentum components of $N(E_F)$ are 6, 17, 64 and 13% for s, p, d and f compared to 4, 16, 67 and 13% for FCC. The larger s content in DHCP indicates more free-electron-like Fermi surface properties such as larger Fermi velocity. However, the root mean square variations are larger in DHCP than in FCC.

3.3. Fermi surface properties

The results for the volume dependence of several properties are summarised for the FCC phase in table 1 and for the DHCP phase in table 2. v_F is the Fermi velocity and ω the plasma frequency. P is the calculated pressure. γ is the calculated electronic specific heat coefficient, equal to $N(E_F)(1 + \lambda)$ without consideration of spin fluctuations and with $\gamma^{sf} = N(E_F)(1 + \lambda + \lambda_{sf})$ when spin fluctuations are included. η is the electronic stiffness.

For the FCC phase we can compare several results with previous calculations. Our results at ambient pressure of $N(E_F)$, v_F, and $\hbar\omega$ are in the range of values calculated

Table 1. Calculated properties for FCC La. Symbols are defined in the text.

$-\Delta V/V$ (%)	$N(E_F)$ (Ryd^{-1}/atom)	v_F (10^7 cm s^{-1})	$\hbar\omega$ (eV)	P (GPa)	λ	T_c (K)	γ (mJ mol^{-1} K^{-2})	$\langle\bar{S}\rangle$	T_c^{sf} (K)	γ^{sf} (mJ mol^{-1} K^{-2})	η (eV Å^{-2})
0	31.0	5.10	6.44	−1.03	1.64	11.4	14.2	0.410	7.5	14.9	4.1
1.5	30.5	5.19	6.56	−0.61	1.68	11.7	14.2	0.40	8.0	14.9	4.2
3.0	30.2	5.28	6.68	−0.17	1.67	11.9	14.0	0.40	8.3	14.7	4.4
4.4	30.0	5.37	6.81	0.33	1.73	12.4	14.2	0.40	8.8	14.8	4.5
5.9	29.7	5.47	6.97	0.76	1.78	12.8	14.3	0.40	9.2	15.0	4.6
7.3	29.4	5.58	7.12	1.20	1.82	13.2	14.4	0.39	9.7	15.0	4.8
10.1	28.3	5.76	7.34	2.07	1.77	13.4	13.6	0.37	10.2	14.1	5.0
14.3	26.6	6.13	7.74	3.74	1.70	13.7	12.5	0.35	10.9	12.9	5.3
18.3	25.7	6.48	8.24	5.65	1.76	14.5	12.3	0.34	11.9	12.7	5.7
22.1	24.8	6.84	8.76	7.57	1.87	15.5	12.3	0.33	13.2	12.7	6.1

T_c and γ have been calculated without spin fluctuations, T_c^{sf} and γ^{sf} with spin fluctuations.

Table 2. Calculated properties of DHCP La. Symbols are defined in the text.

$-\Delta V/V$ (%)	$N(E_F)$ (Ryd^{-1}/atom)	v_F (10^7 cm s^{-1})	$\hbar\omega$ (eV)	P (GPa)	λ	T_c (K)	γ (mJ mol^{-1} K^{-2})	$\langle\bar{S}\rangle$	T_c^{sf} (K)	γ^{sf} (mJ mol^{-1} K^{-2})	η (eV Å^{-2})
0	28.9	3.00	3.63	−0.79	1.58	11.1	12.9	0.38	8.0	13.5	3.9
1.5	26.6	3.09	3.64	−0.37	1.49	10.6	11.5	0.35	8.1	11.9	3.8
3.0	25.4	3.17	3.67	0.05	1.43	10.2	10.7	0.34	8.0	11.1	3.7
4.4	24.1	3.27	3.71	0.50	1.35	9.9	9.8	0.32	7.9	10.1	3.7
5.9	23.7	3.32	3.78	0.99	1.34	10.0	9.6	0.31	8.1	9.9	3.7
7.3	23.1	3.37	3.81	1.49	1.32	9.9	9.3	0.31	8.1	9.5	3.8
(10.1	21.9	3.49	3.90	2.56	1.28	9.9	8.7	0.29	8.4	8.9	3.9)
(14.3	19.6	3.65	3.95	4.19	1.22	9.8	7.6	0.26	8.5	7.7	3.9)
(18.3	15.8	4.04	4.02	6.01	1.03	8.0	5.5	0.21	7.0	5.6	3.4)
(22.1	14.9	4.18	4.15	7.96	1.05	8.5	5.3	0.20	7.6	5.4	3.4)

T_c and γ have been calculated without spin fluctuations, T_c^{sf} and γ^{sf} with spin fluctuations. Values within parentheses refer to hypothetical DHCP La, unstable at these pressures.

previously by other authors (Glötzel and Fritsche 1977, Glötzel 1978, Glocker and Fritsche 1978, Pickett *et al* 1980). Our result for η of 4.1 eV Å^2 is somewhat larger than previous results of 3.12 (Glocker and Fritsche 1978), 2.9 (Glötzel 1979), or 2.6 eV Å^2 (Pickett *et al* 1980). The lower value obtained from LAPW (2.6) is probably due to smaller s, p and f components in their $N(E_F)$ values. Our DOS values increase especially p–d and d–f scattering due to the region between MT and WS spheres. Such interstitial regions do not contribute to η in LAPW and our value of η is therefore larger.

Using our method to repeat the calculations at several fairly closely spaced lattice constants enables more reliable estimation of the pressure dependence of several Fermi surface properties. In the zero-pressure limit we obtain the following results for the FCC phase: $\mathrm{d}\ln N(E_F)/\mathrm{d}\ln V = 0.8$, $\mathrm{d}\ln v_F/\mathrm{d}\ln V = -1.25$ and $\mathrm{d}\ln \eta/\mathrm{d}\ln V = -2.13$. For the plasma frequency it is convenient to describe its pressure dependence by a parameter q defined by Neve *et al* (1983).

$$\omega^2(V) = \omega^2(V_0)/(1 + q\Delta V/V_0). \tag{2}$$

An advantage with this definition is that it gives $q = 1$ for free electrons at all pressures and thus does not rely on a low-pressure limit. From the results in table 1 we get $q = 2.5$. This is an unusually large value, by far the largest among several superconducting and non-superconducting elements investigated previously where q ranges from 0.35 for Al to 1.95 for Nb (Sundqvist *et al* 1985).

These results are in agreement with the trend obtained from the few calculations at reduced lattice parameters that are available in the literature. From Dakshinamoorthy and Iyakutti (1983) the initial change of $\mathrm{d}\ln N(E_F)/\mathrm{d}\ln V$ is about 1. Pickett *et al* (1980) report a reduction in $N(E_F)$ of 20% and an increase in v_F of almost 40% at 16% volume reduction. Both of these changes have the same sign as our results but are larger or much larger. For q, the data by Pickett *et al* are consistent with a value in the range 2.3–2.8, confirming a large value of this parameter in the FCC phase of La. As for η, in spite of the large differences in zero-pressure values, the volume dependence is similar with $\mathrm{d}\ln \eta/\mathrm{d}\ln V = 2.4 \pm 0.1$, from Pickett *et al* (1980) and 2.1 from Glötzel (1978), using the compressibility of Vaidya and Kennedy (1970).

For the DHCP phase, the Fermi surface properties are in many respects remarkably different. At ambient pressure $N(E_F)$ and η are both somewhat smaller and v_F and ω considerably smaller than in the FCC phase.

These differences are even more pronounced when the pressure dependence is considered. v_F increases faster and $N(E_F)$ decreases much faster than in the FCC phase with the initial rates of $\mathrm{d}\ln v_F/\mathrm{d}\ln V = -1.8$ and $\mathrm{d}\ln N(E_F)/\mathrm{d}\ln V = 4$. The increase of the plasma frequency with pressure is much slower and almost free electron-like with $q \simeq 1.2$, and in contrast to the large increase of η in the FCC phase, there is at most a small variation in the DHCP phase, with an initial decrease of η, $\mathrm{d}\ln \eta/\mathrm{d}\ln V$ being about 1.5.

By plotting the volume dependence of the calculated Fermi surface properties one observes that in the DHCP phase at a volume compression of about 6% there is a change of slope in $N(E_F)$ and v_F, a change of sign of the slope of η, and possibly a small discontinuity in ω. Although such anomalies are no definite sign of a phase transition, it is tempting to associate them with an iso-electronic phase transition at about 2 GPa as discussed in § 2.4. It should be noted, however, that this feature is observed in both phases in the experiments and only in the DHCP phase in the calculations. Changes in topology at the Fermi surface are possible in the rather complex DHCP Fermi surface.

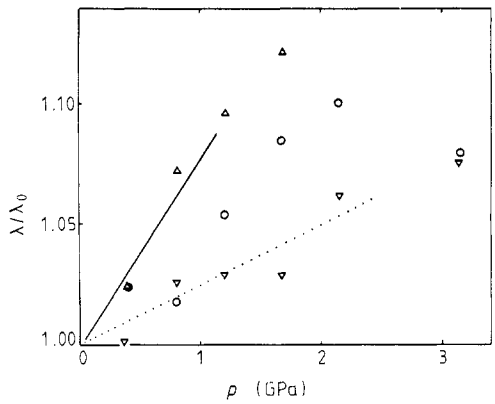

Figure 8. Summary of the results for the pressure dependence of λ in the FCC phase. $\triangle$, $\lambda \sim \eta$ ($\gamma_G = 0$); ∇, from η ($\gamma_G = 0.7$); $\bigcirc$, from η and equation (3). Full line, equation (6) with $q = 2.5$; dotted line, equation (8) with $q = 2.5$.

For instance, in figure 6 it can be seen that the H and K points have bands near E_F at ambient pressure while at 14% volume reduction these bands are above E_F.

4. Superconductivity and related properties

4.1. λ and its pressure dependence

Our results give two independent estimates of λ and its pressure dependence for each phase of La. One is from the band structure calculation of η and the scaling of the phonon frequencies. The other method uses a combination of resistivity measurements and the calculation of the plasma frequency. These results are now separately described.

4.1.1. $\lambda(p)$ from band results. The electronic part η of $\lambda = \eta/M\langle\omega_{ph}^2\rangle$ is calculated in the rigid ion approximation directly from the band results. As is usual we take for the phonon part $\langle\omega_{ph}^2\rangle = 0.5\,\theta^2$ which typically leads to acceptable results (Papaconstantopoulos *et al* 1977). At reduced volumes we scale the phonon spectrum through the calculated compressibility as in the low q-limit:

$$\theta(p) = \theta(0)[r(p)/\kappa(p)]^{1/2} \tag{3}$$

where κ is the compressibility and r the Wigner–Seitz radius at the given volume. This scaling has proved to be useful in some cases (Pictet *et al* 1987), but it does not take into account any softening of special q modes. Therefore phonon anomalies, such as has been observed in La (Stassis *et al* 1985) and which are important for the FCC–DHCP transition, cannot influence our results for λ. On the other hand it is probable that softening of a few q modes will not be very important for the total λ, which depends on an average for all modes.

In figure 8 we show $\lambda(p)$ variations assuming extreme values for the $\theta(p)$ variation in the FCC phase. Writing

$$\theta(p) = \theta(0)(1 + \gamma_G \kappa p) \tag{4}$$

we first take the Grüneisen constant $\gamma_G = 0.7$, corresponding to the (surprisingly) high average room temperature value (Gschneidner 1964), and secondly, assume no pressure variation of θ. We then obtain the two extremal $\lambda(p)$ dependences of figure 8. With our calculation from (3) we obtain intermediate values.

Table 3. Analysis of $R(p, T)$.

	Equation (5)			Equation (7)			
	A (10^{-3} K^{-1})	B (10^{-2} GPa^{-1})	10^4 RMS	a (10^{-3} K^{-1})	b (10^{-2} GPa^{-1})	c (10^{-3} K^{-1})	10^4 RMS
FCC	2.29	−1.04	7.0	2.37	−0.97	13.4	4.8
DHCP	2.47	−0.74	6.8	2.51	−0.73	9.6	3.8

The result for $\lambda(p)$ in the DHCP phase, using (3), is strikingly different. The reduction of λ with p is appreciable as seen in table 2. This is mostly due to the relatively more rapid decrease of $N(E_F)$ and η with pressure.

Independent estimates of λ exist for the FCC phase at zero pressure; such as 0.96 (Dakshinamoorthy and Iyakutti 1983), 1 (Baquero and Lopez-Olazagasti 1984), 1.3 (Glötzel 1978) and 1.42 (Pickett *et al* 1980). From the specific heat γ in the FCC and DHCP phases, 11.5 and 9.4 mJ mol^{-1} K^{-2} (Johnson and Finnemore 1967), together with our $N(E_F)$ values, one obtains $\lambda = 1.14$ and 0.88, respectively. Our calculated values are in the upper end of these variations.

4.1.2. $d\lambda/dp$ from $R(p, T)$ and ω. In this method one uses the parameter q describing the pressure dependence of ω, and the logarithmic pressure dependence, B, of dR/dT, which can be evaluated from the experimental $R(p, T)$ by a fit to

$$R(p, T) = R_0(1 + AT)(1 + Bp). \tag{5}$$

T varies in an interval around 0 °C, and is therefore expressed in centigrade. With the assumption that $d\lambda/dp = d\lambda_{tr}/dp$, where λ_{tr} is the electron–phonon transport coupling, one then finds (Neve *et al* 1983, Sundqvist *et al* 1985)

$$d \ln \lambda/dp = B + \kappa(q - \tfrac{1}{3}). \tag{6}$$

La, however, is exceptional among the 10 elements studied by this method, since the pressure coefficient of resistance varies quite strongly with temperature also in the limited interval from −20 to 20 °C. This leads to larger relative root mean square deviations (RMS) in (5) than expected for well-behaved metals. Nor can one use results such as those in figure 2 directly in the calculation of $d\lambda/dp$, due to the strong temperature dependence of R (Rapp 1978). We therefore also investigated the possibility of an unusual temperature dependence of B in (5) by fitting the same data to

$$R(p, T) = R_0(1 + aT)[1 + bp(1 + cT)]. \tag{7}$$

Taking the logarithmic pressure derivative of dR/dT at $T = 0$ °C, the midpoint of the measuring interval, one finds that (6) should be replaced by

$$d \ln \lambda/dp = b(1 + c/a) + \kappa(q - \tfrac{1}{3}). \tag{8}$$

The results from the analyses of $R(p, T)$ are shown in table 3. The quality of the fits are significantly improved by using (7) as compared to (5). This is natural since an additional fitting parameter is used, but nevertheless gives some support for the physical relevance of (7) for La.

In figure 8 we show the results for $d \ln \lambda/dp$ from both (6) as well as (8) for FCC La. The difference between these two results may be taken as an illustration of the unusually

large uncertainty of this method in the present case. Each of the two independent methods used to evaluate λ meet with unusual complications when applied to La. Nevertheless, the results, although somewhat scattered, are quite consistent. All data in figure 8 can be summarised as $d \ln \lambda / dp = (5 \pm 2) \times 10^{-2}\,\mathrm{GPa}^{-1}$. This agreement between very different methods strengthens our results.

For the DHCP phase the results for $\lambda(p)$ are not conclusive. From (6) we obtain $d \ln \lambda / dp = 2.8 \times 10^{-2}\,\mathrm{GPa}^{-1}$ and from (8), λ = constant. The result for λ from table 2, on the other hand, suggests a strong decrease of λ with pressure. Even if an average phonon frequency is assumed to be pressure independent, a weak decrease of λ with pressure is suggested from the results for η. However, both of these methods support the conclusion that there is a substantial difference between the pressure dependence of λ in the two phases.

4.2. Spin fluctuations

The results for $\lambda(p)$ of the preceding section cannot fully explain $T_c(p)$ of FCC La and fail in the case of DHCP La. The results in tables 1 and 2 show this for the moderate lattice stiffening of (3).

The values of λ_{sf} for the two phases, calculated as described in § 3.1, decrease with pressure because of the dependence of $N(E_F)$, which decreases as well. The decrease is faster in DHCP La than in FCC La. By a normalisation of λ and μ^*, values of T_c^{sf} are calculated using a modified McMillan equation (Daams *et al* 1981) and the same electron–phonon coupling as before. The increase of T_c^{sf} is now more evident for FCC La (table 1) and agrees reasonably well with the experimental rate of increase (Maple *et al* 1969). For DHCP La, T_c^{sf} is almost constant when the band calculation of λ is used (table 2) and again agrees reasonably with observations when we use the experimentally based λ values. The magnitude of $T_c^{sf}(0)$ agrees better than $T_c(0)$ with experiment (5–6 K) for both phases.

Our way of including spin fluctuations in the understanding of the T_c variations is fairly rough and quantitative results should not be stressed. But it shows qualitatively that spin fluctuations, which gradually disappear with pressure, can explain an increase of T_c with pressure. It is important to note that this result was obtained assuming a phonon spectrum which shows (normal) moderate stiffening with increasing pressure. This explanation of the increase of T_c therefore provides an alternative to the often claimed explanation due to a general lattice softening. Similar and even more important influences of spin fluctuations on T_c than found here for La have been established for V at zero pressure (Rapp and Crafoord 1974, Rietschel and Winter 1979), and under pressure (Sundqvist *et al* 1985) and for Nb–Zr alloys at $p = 0$ and $p > 0$ (Pictet *et al* 1987).

5. Summary and concluding remarks

We have studied the electrical resistance and band structure of both FCC and DHCP La from several aspects which are related to T_c and the increase of T_c with pressure in both phases.

In the analysis of the experiments we have stressed the importance of hydrostatic conditions for resistance measurements under pressure. This is particularly important for La where the FCC phase is only metastable under low pressure, while simultaneously the DHCP phase can be transformed into the FCC phase by deformation or cold-work

(Balster and Wittig 1975). By hydrostatic measurements on several samples of both phases we have now verified that the pressure coefficient of resistivity is negative in both structures in the whole temperature region from 170 to 300 K. Furthermore, we have found that the pressure and temperature dependence of the resistance in both phases are comparatively similar, with fairly small and negative values of the parameter B in (5), as is usual for transition metals (Sundqvist *et al* 1985).

The band structure calculation of FCC La at ambient pressures gave results which are in fairly good agreement with published results. For the DHCP phase it appears that there are no previous calculations. For the calculated Fermi surface properties we find large differences between the two phases, particularly in regard to the stronger pressure dependence of DHCP La.

La shows a number of anomalous properties some of which were mentioned in the introduction. Two such anomalies are obtained from our results: (i) the unusually large temperature dependence of the pressure coefficient of resistance, and (ii) the exceptionally strong increase of the plasma frequency with pressure in the FCC phase. In the DHCP phase, on the other hand, the change of the plasma frequency is almost free-electron-like.

From the measurements and the calculations we can estimate the pressure dependence of λ in two independent ways. For the FCC phase both methods confirm that λ increases with pressure at a rate within $\mathrm{d}\ln\lambda/\mathrm{d}p = 0.05 \pm 0.02\ \mathrm{GPa}^{-1}$. From the calculations one would describe this as mainly due to the increased electronic stiffness η, while, from combining the experiments and ω, the same effect arises due to the strong pressure dependence of ω. For the DHCP phase both methods suggest a smaller $\mathrm{d}\lambda/\mathrm{d}p$, but with strikingly different values. From η and θ we find a strong decrease of λ, while the results from $R(p, T)$ and ω indicate $\mathrm{d}\ln\lambda/\mathrm{d}p = 0.015 \pm 0.015\ \mathrm{GPa}^{-1}$.

These results and the high values of $N(E_F)$ in both phases point at the possibility that spin fluctuations are of importance in La. Our simplified calculation confirms this. λ_{sf} decreases slowly with pressure for the FCC phase and quite strongly for the DHCP phase. Rough estimates indicate that these changes are of the order required to account for the observed $T_c(p)$ together with the results for $\lambda(p)$ from both methods for FCC La and from $R(p, T)$ and ω for DHCP La.

Some shortcomings and remaining problems have already been mentioned, such as how to interpret the strong temperature dependence of B' in terms of our model for $\mathrm{d}\lambda/\mathrm{d}p$. Another question is why the resistive properties are similar in both phases, while results from the band structure calculations related to transport properties are so different? A point of concern is the unknown sensitivity of the band structure calculation to the assumption that c/a of the DHCP phase is independent of pressure. The fact that E_F is close to a peak in the density of states makes the $N(E_F)$ values more uncertain and may explain some of the less satisfactory comparisons between theory and experiment for the DHCP phase.

Our results predict that there should be a large difference in the electronic Grüneisen constant γ_e between the two phases. From the pressure dependence of $N(E_F)$ and λ, we expect a value close to 0 for the FCC phase and a large and positive value of γ_e for the DHCP phase. It would seem that the only available experimental low-temperature result is a rough value of -2 for the FCC phase (Barron *et al* 1980).

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