Effect of pressure on the superconducting T_c of lanthanum

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The effect of pressure on the superconducting transition temperature T_c of La was studied up to 50 GPa. $T_c(P)$ shows a rather complicated variation with a discontinuous increase in T_c at about 2.2 GPa due to the first-order phase transition from dhcp to fcc structure. At about 5.4 GPa a sharp peak is observed due to the soft-mode phase transition from fcc to the distorted fcc structure and two broad maxima are found within the stability region of the distorted fcc structure around 12 and 39 GPa. Some differences between these and previous low-pressure data for metastable fcc La are noticed. The results are discussed in connection with pressure-induced structural phase transitions found in earlier x-ray-diffraction experiments and band-structure calculations giving evidences for van Hove singularities in the density of states.

It is well known that the superconducting transition temperature T_c of lanthanum metal increases strongly with increasing pressure and reaches almost 13 K at about 17 GPa.[1,2] Thereby $T_c(P)$ exhibits some anomalies at about 2.5, 5.3, and 17 GPa. The first two anomalies were attributed to structural phase transitions. According to band-structure calculations, the structural stability in rare-earth metals is controlled by the d-electron number which increases under pressure due to the s-d transfer.[3–5] Therefore, in addition to the influence of pressure-induced structural transitions on T_c, the fine structure of the density of states could also be reflected in $T_c(P)$ through such pressure tuning of the d band. The predicted van Hove singularities (VHS) in the density of states are of particular interest in this respect. Moreover, it is worth noting that most previous $T_c(P)$ data for La were obtained in the fcc phase which is metastable below about 520 K at ambient pressure. For metastable fcc-La $T_c(P)$ is found to be about 1 K higher than for the thermodynamically stable double hcp (dhcp) phase. The present paper reports $T_c(P)$ data for dhcp-La up to 2 GPa and for the fcc and distorted fcc phase up to 50 GPa which extends considerably the pressure range ($p<27$ GPa) of previous investigations.[1,2]

High pressures were generated with a diamond anvil cell made from a nonmagnetic alloy. To decrease the inductive coupling between the coil systems used for ac susceptibility measurements and the metallic surroundings, the diamond anvils with 0.5 mm culet diameter are mounted on sapphire backing plates. NiMo-alloy gaskets with an initial thickness of 300 μm preindented to 60 μm are used, and the sample with typical dimensions $80\times80\times30$ μm is placed together with small ruby chips in a gasket hole of 150 μm in diameter. The La sample material was provided by Gschneidner, Jr. with chemical analysis[6] giving as major impurities 540 ppm fluorine, 300 ppm oxygen, 275 ppm hydrogen and less than 20 ppm iron. A methanol-ethanol mixture in the ratio 4:1 served as pressure-transmitting medium. The cell was cooled down to 4.2 K in a glass dewar and the temperature was measured by a Cu-Fe/Cu thermocouple with an accuracy of ±0.2 K. The pressure was determined from the shift of the R_1 ruby fluorescence line using the nonlinear scale at room temperature[7] after each cycle of cooling the cell under pressure down to 4.2 K. Reasons for adopting this procedure for the pressure determination at low temperatures have been discussed in detail previously.[8] The superconducting transition was detected by measuring the ac magnetic susceptibility as a function of temperature. Data were taken only on heating cycle. Two twin coil systems are used as part of a bridge. One of these coil systems is positioned symmetrically around the anvils and the reference system is placed nearby. After additional compensation, the signal from the secondary coils is monitored by a lock-in amplifier. Thereby T_c is defined as midpoint of the susceptibility change.

Figure 1 shows the present data for the effect of pressure on T_c of La together with the previous results for the stable dhcp phase at $P<2$ GPa as well as data for the initially metastable fcc phase.[2] The present T_c data at pressures up to 2 GPa are in good agreement with the earlier values for dhcp La, as can be seen in Fig. 1. However, in the present experiments there is a large step in T_c at 2 GPa which was not observed previously. This step indicates that at pressures above 2 GPa the sample has transformed to the stable fcc modification.[9] Moreover, a rather narrow λ shaped cusp is found at 5.4 GPa instead of the broad structure at 5.3 GPa in the previous study. It is noticed that the maximum value of T_c of this cusp depends on the history of the pressure application. A broad maximum in T_c is observed around 12 GPa as in the previous experiments; however, the pressure value for this maximum is slightly different from the previous value of 17 GPa. This difference can be explained by metastabilities, impurities, and larger pressure gradients in the previous studies. In addition, the present data show a second broad maximum of T_c in the extended pressure range around 39 GPa.

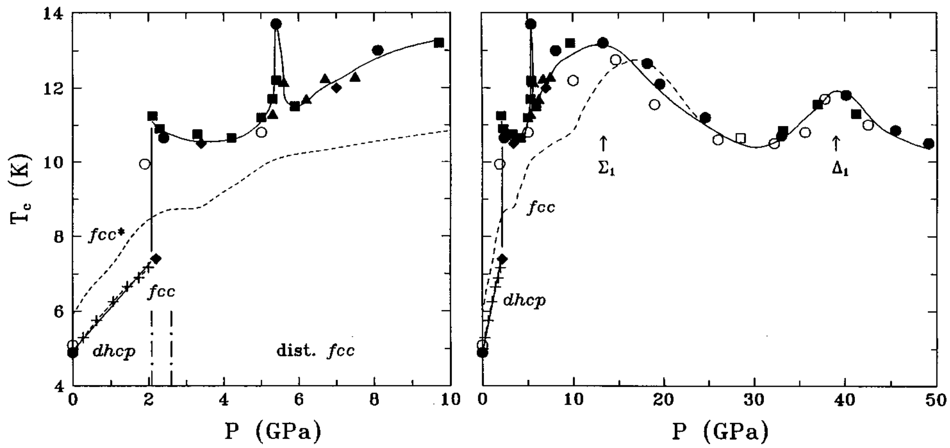

FIG. 1. Pressure dependence of T_c in La. Dark and open symbols denote the data obtained in pressure increasing and releasing runs, respectively. Solid lines are guides to the eye. The data from Ref. 2 for the dhcp and the "fcc" phases are shown by crosses and dashed lines, respectively, and fcc* denotes the previous data for metastable fcc samples. Arrows labeled Σ_1 and Δ_1 indicate the pressures where these states cross the Fermi level according to Ref. 12.

Obviously, some of the anomalies in T_c are simply related to phase transitions occurring in La under pressure. Unfortunately, all the structural studies on La under pressure have been performed only at 200 K and above,[6,10] showing the following sequence of phase transitions in La under pressure at room temperature: dhcp–fcc–distorted fcc–fcc in the previously investigated pressure range up to 67 GPa.[10] Extrapolation of the corresponding phase boundaries to zero kelvin resulted only in rough estimates for the corresponding equilibrium transition pressures[1,6,9–11] with a value of 2 GPa for the dhcp–fcc transition with a very large uncertainty due to the large region of metastability for this first-order reconstructive transition and with the values 2.5(5) and 90(20) GPa for the almost second order phase transition from fcc to distorted fcc and back to fcc, respectively. Together with the results of the resistivity measurements on La under pressure in a wide temperature range,[1] one can attribute the discontinuous increase of T_c at about 2.2 GPa to the phase transition from dhcp to fcc structure. The second anomaly at about 5.4 GPa is located significantly above the (extrapolated) value for the fcc–distorted fcc transformation, which shows that a direct correlation with a structural transition cannot be made for this feature at the present time. Also the broad maxima of T_c around 12 and 39 GPa cannot be assigned to any known structural transition in La. One can note, however, that these pressure values are close to those where the Fermi energy ϵ_F crosses due to the s-d transfer under pressure van Hove singularities (VHS) to Σ_1 and Δ_1 levels according to band-structure calculations for fcc La,[12] and one can expect that the change of the Fermi surface topology at these singularities should result in electronic Lifshitz transitions of 5/2 order with particular anomalies in the bulk modulus.[13] In addition, the electron-phonon coupling should lead to peculiarities in the phonon spectrum when the VHS passes through ϵ_F.[14] In principle, both features may cause lattice instabilities. However, it is not clear which kind of lattice distortions should be expected in the present case. One can only note that the energetic location of the van Hove singularity $\epsilon_{\rm VHS}$ must move away from ϵ_F in order to induce an isostructural transition in a simple model.[13] The pressures needed to shift $\epsilon_{\rm VHS}$ to ϵ_F and to induce a structural transition are therefore generally different. Nevertheless, there is some evidence in favor of a correlation between the two phase transitions below 10 GPa and the two changes in the Fermi surface topology found in band-structure calculations for fcc La.[15]

If the VHS is located at the maximum of the peak in the density of states $N(\epsilon)$, and this is anticipated for the saddle point singularity, the behavior of $T_c(P)$ around the VHS can be qualitatively understood through a variation of $N(\epsilon_F)$ under pressure, if one takes into account that T_c and $N(\epsilon_F)$ are related to each other in the McMillan theory for strong-coupled superconductors[16] through electron-phonon coupling constant λ given by

$$\lambda = N(\epsilon_F)\langle I^2\rangle / M\langle\omega^2\rangle, \tag{1}$$

where $\langle I^2\rangle$ is the average of the squared electron-phonon matrix element, M is the atomic mass, and $\langle\omega^2\rangle$ is the average of the squared phonon frequency. Since T_c increases monotonically with increasing λ and $N(\epsilon_F)$, its pressure dependence should follow the variation of $N(\epsilon_F)$ which, in turn, should change due to the shift of ϵ_F under pressure. This picture would correspond to the idea that the pressure dependence of T_c in d metals and their compounds is mainly governed by the shape of the electronic density of states curve, and this simple picture may be reasonable also in the present case. In fact, band-structure calculations show only a small increase of $\langle I^2\rangle$ in La under pressure[15] and far away from any phase transition one expects that increasing pressure stiffens the lattice and increases $\langle\omega^2\rangle$. These two changes may cancel each other to some extent in Eq. (1), but any anomaly in the electron-phonon coupling $\langle I^2\rangle$ could directly affect T_c in the observed way. Further experimental and theoretical studies on the volume dependence of different parameters which determine T_c in this way are needed to give a more quantitative account of the special behavior observed for $T_c(P)$ of La in this extended range of pressures.

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