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Pressure Effect on the Magnetic Properties of Superconducting La and La-Ce

Mitsuhiro TAKATA* and Soichi OSHIDA

Faculty of Engineering Science, Osaka University
Toyonaka, Osaka

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The pressure dependence of the thermodynamic critical field of La has been measured, and calculated the pressure effect on the electronic density of states at the Fermi surface is calculated.

The value of $d\ln N(0)/d\ln v$ is found to be -4.54 ± 1.67, where $N(0)$ and v are the density of states at the Fermi surface and the volume respectively.

From the pressure dependence of $N(0)$ and T_c of La-1.0% Ce, $d\ln J/d\ln v$ is calculated to be -4.3 (J is the exchange interaction parameter). From the experimental result, the mechanism of superconductivity of La at high pressure is discussed.

§ 1. Introduction

Lanthanum is the only element in groupe IIIB of the periodic table which is a superconductor and does not have any 4f-electrons, but the next element Ce, which is not a superconductor, has one 4f-electron. For this reason it was suggested that La has an f-band just above the Fermi level and virtual excitation of electrons into the f-band can strongly enhance the superconductivity.[1] In addition, the marked peculiarity of La is the noticeable increase of transition temperature (T_c) upon application of pressure which has been attributed to the peculiarities of the band structure.[2,3]

The electronic specific heat measurement offers the important information for the electronic energy states of metals, but experimentally it is very difficult to obtain the specific heat data at high pressure.[4]

Fortunately it is possible to deduce the electronic specific heat coefficient from the knowledge of the limiting temperature variation of thermodynamic critical field (H_c) as the temperature approaches to 0°K.[5]

We present here the result of the critical field measurement of La and discussed the origin of the enhancement of superconductivity at high pressure.

Further we note the marked initial decrease of transition temperature with pressure[6] when the cerium impurity is added to La. This has been attributed to the magnetic impurity level near the Fermi level of La.[6] Therefore the pressure dependence of H_c and T_c of La-Ce alloy should give information about the energy band behaviour near the Fermi level with pressure. Here we measured the pressure dependence of H_c of La-1.0 % Ce and discussed the contribution of 4f-level to the superconductivity of La.

§ 2. Experimental

2.1. *Sample preparation*

The starting materials were 99.98% La and 99.98 % Ce obtained from Johnson-Massay and Co.

The α-phase samples used in this experiment were prepared by filing the bulk forms into the powder of about 100μ in diameter, and subsequent annealing at 200°C for one month.[7]

The powdered samples showed more reversible magnetization curves than that of bulk samples.[7,8] Typical magnetization curve of La in powder form at 4.2°K is shown in Fig. 1.

2.2. *Procedure*

The method of generating high pressure and magnetization measurement were the same as that previously described.[9]

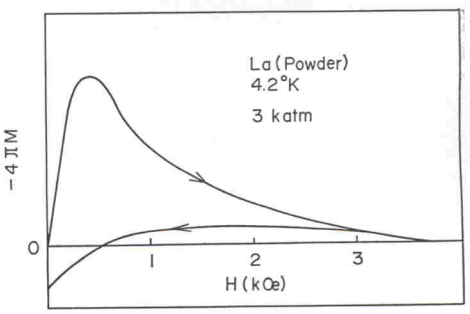

Fig. 1. Magnetization curve of powder La in increasing and decreasing external field.

* Present address: Sumitomo Special Metals Co., Ltd. Yamazaki Works, Simamoto-cho, Mishima-gun, Osaka.

After the magnetization measurement at normal pressure, the high pressure up to 5,000 atom was apllied and the measurement was done. And then the pressure was released. The critical field and transition temperature at final stage showed no difference from the initial data within the experimental error.

The data used in the following analysis were taken as follows. At first the high pressure was apllied at room temperature and then cooled down to liquid He temperature for the magnetization measurement in superconducting state. Then the pressure was released at room temperature and immediately cooled down for the measurement at normal pressure.

As the magnetization of the pressure bomb was very large at high external field, the upper critical field (H_{c2}) of La could not be accurately determined. The inaccuracy of H_{c2} did not actualy effect the value of thermodynamic critical field (H_c), because the magnetic moment near H_{c2} was much smaller than that near the first critical field (H_{c1}).

§ 3. Result and Discussion

3.1. Pure La

Practical magnetization curve of La at 1.58°K was shown in Fig. 2. These magnetization curve were taken at increasing field. The upper and lower critical field and the magnetization increased with pressure at any temperature below T_c. (For most superconductors both T_c and H_c decrease with pressure.)

Thermodynamic critical field was calculated from magnetization curves in the increasing external field H, that is,

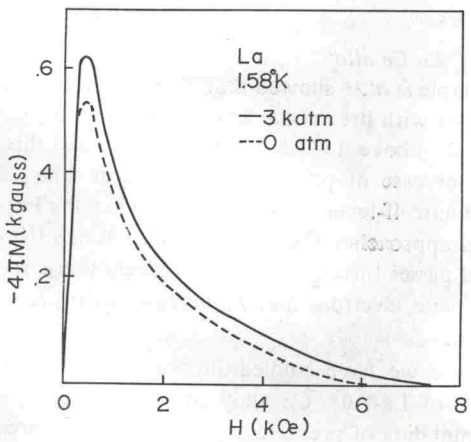

Fig. 2. Magnetization curve of powder La in increasing external field at different pressures.

$$\frac{H_c^2}{8\pi} = -\int_0^{H_{c_2}} M dH \qquad (1)$$

where M is the magnetization of specimen in the superconducting state.

The temperature dependence of the thermodynamic critical field thus obtaind for powdered La was plotted in Fig. 3. The value of H_0 (critical

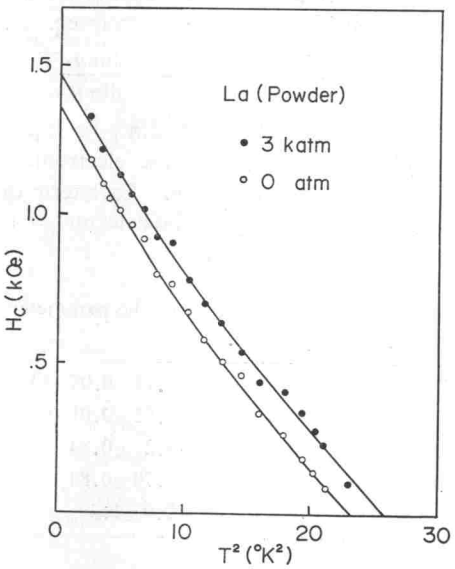

Fig. 3. Temperature dependence of thermodynamic critical field of La at different pressures.

field extrapolated to 0°K) at normal pressure was higher than the value of another magnetic measurement[7] and the calculated value from specific heat measurement.[10] The irreversibility of magnetization curve increased with the size of particles. For the bulk samples the simple integration of eq. (1) in the case of increasing external field gave a very large thermodynamic critical field. However, it was very difficult to get enough sensitivity for smaller particles, since the total volume of the specimen was limited by the size of the pressure bomb.

In contrast to the magnetic parameters, T_c was not effected by the sample sizes.

The powder sample cited in Fig. 3 has an average diameter of about 100 μ, and is annealed at 200°C in a vacuum of 2×10^{-5} mm Hg for about one month. The magnetization curve in the increasing and decreasing field was already shown in Fig. 1.

On the basis of thermodynamic equation for superconductors, we can deduce the coefficient of electronic specific heat per unit volume $\gamma^*(=\gamma/v$, where v is the volume) from the knowledge of H_c

at sufficiently low temperatures,[9,10] that is,

$$\frac{H_c(t)}{H_0}=1-a_2t^2 \qquad (2)$$

and

$$a_2=2\pi\gamma^*\frac{T_c^2}{H_0^2} \qquad (3)$$

where $t=T/T_c$.

We can deduce the volume dependence of the electronic specific heat coefficient from eq. (3).

$$\frac{\mathrm{dln}\,\gamma^*}{\mathrm{dln}\,v}=2\frac{\mathrm{dln}\,H_0}{\mathrm{dln}\,v}-2\frac{\mathrm{dln}\,T_c}{\mathrm{dln}\,v}+\frac{\mathrm{dln}\,a_2}{\mathrm{dln}\,v} \qquad (4)$$

As is well known, $\mathrm{dln}\,\gamma^*/\mathrm{dln}\,v$ is equal to $\mathrm{dln}\,N(0)/\mathrm{dln}\,v$, where $N(0)$ is the electronic density of states at the Fermi level. Each term in the right-hand side of eq. (4) can be determined from magnetization measurement.

Table I. Pressure dependence of the parameter appeared in eq. (4) for La.

T_c(°K)	5.15±0.05 (3 kbar) 4.82±0.01 (0 kbar)
$\mathrm{dln}\,T_c/\mathrm{dln}\,v$	−6.27±0.84
$\mathrm{dln}\,H_c/\mathrm{dln}\,v$	−7.70±0.84
$\mathrm{dln}\,\gamma^*/\mathrm{dln}\,z$	−2.9±1.4

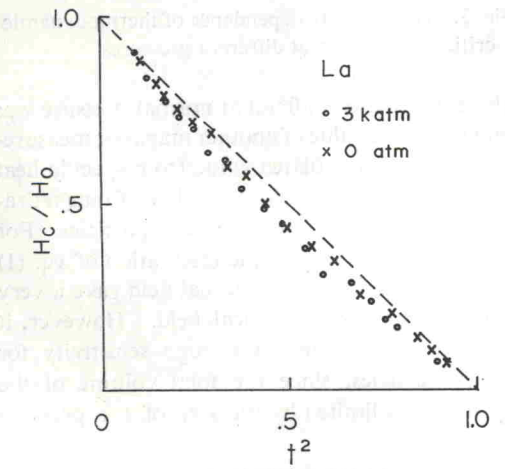

Fig. 4. Reduced critical field vs. reduced temperature of La.

The experimental results for La are listed in Table I, where we used the value of compressibility of 4.2×10^{-12} cm/dyn. We could not observe the change of a_2 with pressure within the experimental error, as shown in Fig. 4. To calculate the value of $\mathrm{dln}\,\gamma^*/\mathrm{dln}\,v$, we assumed $\mathrm{dln}\,a_2/\mathrm{dln}\,v\cong0$,[11] but this parameter is important for the discussion of electron-phonon interaction. To obtain the value of $\mathrm{dln}\,a_2/\mathrm{dln}\,v$, it is necessary to increase the accuracy of measurement of $H_c(T)$ at high pressure.

As shown in Fig. 4, the deviation from linear relation between the reduced critical field and reduced temperature is the same sense as that of reference 10.

Very large negative value of $\mathrm{dln}\,\gamma^*/\mathrm{dln}\,v$ indicates that the application of pressure on La increases the electronic density of states at the Fermi-level.

To explain the increase of T_c with pressure, Ratto *et al.*[3] considered that the electrons in a slightly occupied 4f-level just above the Fermi level depresses the superconductivity of La and the application of the pressure removes the 4f-level away from the Fermi level enhancing the superconductivity. But it is difficult to explain the large increase of γ with pressure by the transfer of small amount of 4f-electrons to the conduction band. And it is also difficult to explain the fact that T_c continuously increases with pressure as high as 140 kbar.[12] (The rapid shift of 4f-level with pressure was observed in La-Ce alloy as described later.)

The mechanism of superconductivity of La suggested by Kuper *et al.* and Kondo[1] is consistent with the sign of $\mathrm{dln}\,V/\mathrm{dln}\,v$,[8] where V is the effective electron-electron interaction parameter in the BCS expression, but there has not been any discussion concerning the pressure dependence of electronic density of states based on these models.

Therefore we conclude that a gradual electronic transition with pressure occurs, that is, s electrons and f electrons (if 4f-band is partialy filled at normal pressure) are transfered to the high density of states energy band (such as the d-band) at the Fermi level with pressure as was discussed in Ce and Cs.[13]

3.2. *La-Ce alloy*

Maple *et al.*[12] showed that T_c of La-2.0% Ce decreases with pressure at first and then it increases rapidly above 15 kbar. They interpreted this as the increase of pair-breaking strength when the magnetic 4f-level of Ce lying just below the Fermi level approaches the Fermi level. When the 4f-level passes through the Fermi level, there is no magnetic electrons and T_c increases with pressure as La.

Here we have studied the pressure dependence of H_c of La-1.0% Ce alloy to obtain the experimental data of pressure dependence of pair-breaking parameter.

For the effect of paramagnetic impurities upon

T_c, the Abrikosov-Gor'kov theory[14] predicts the relationship,

$$T_{cp}=T_c-\frac{1}{4}\pi\tau_s\,,\quad \tau_s\propto J^2N(0) \qquad (5)$$

where T_{cp} and J are the transition temperature of pure metal and exchange interaction parameter between conduction and localized spins, respectively.

Differentiating eq. (5) with respect to pressure, we find

$$\frac{1}{\kappa}\frac{\partial\ln(T_{cp}-T_c)}{\partial P}=\frac{\partial\ln N(0)}{\partial\ln v}+2\frac{\partial\ln J}{\partial\ln v} \qquad (6)$$

where κ is the compressibility. Assuming κ does not change much from the value of $4.2\times10^{-6}\mathrm{atm}^{-1}$ for pure La, we evaluated the parameters in eq. (6) for La-1.0% Ce as shown in Table II. The

Table II. Pressure dependence of the parameter appeared in eq. (4) and (6) for La−1.0% Ce.

T_c(°K)	4.03±0.03 (3 kbar)
	3.82±0.03 (0 kbar)
$\mathrm{dln}\,T_c/\mathrm{dln}\,v$	−4.62±1.05
$\mathrm{dln}\,H_c/\mathrm{dln}\,v$	−6.98±0.62
$\mathrm{dln}\,\gamma^*/\mathrm{dln}\,v$	−5.4±1.7
$-\mathrm{dln}\,(T_{cp}-T_c)/\mathrm{dln}\,v$	−13.9*
$\mathrm{dln}\,J/\mathrm{dln}\,v$	−4.3

* obtained from the initial slope of dT_c/dP vs. (Ce concentration) curve using the experimental results of reference 6 and ours.

value of $\mathrm{dln}\,N(0)/\mathrm{dln}\,v$ is obtained from the pressure dependence of $H_c(T)$ of La-1.0% Ce. Temperature and pressure dependence of H_c are shown in Figs. 5 and 6.

The observed large increase of J with pressure can be interpreted as the rapid approach of magnetic 4f-level to the Fermi level as discussed by Maple *et al.*[12]

Therefore we may conclude that the 4f-level of La (if it can be treated analogously to that of Ce in La) goes away from the Fermi level at high pressure and then the contribution of 4f-level to the superconductivity (if it exists at normal pressure) becomes negligible.

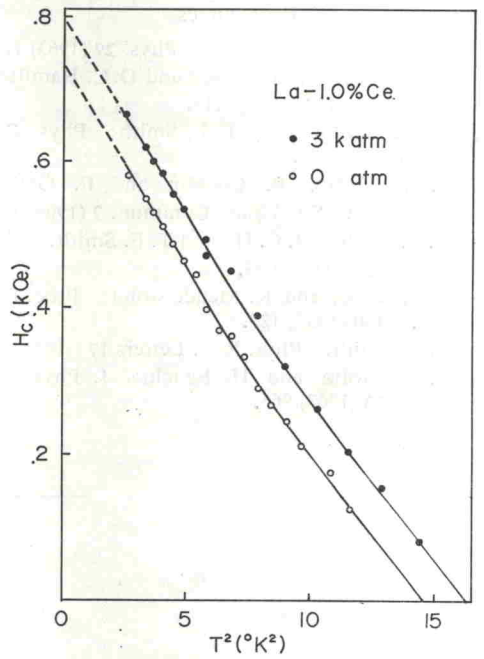

Fig. 5. Temperature dependence of thermodynamic critical field of La−1.0% Ce at different pressure.

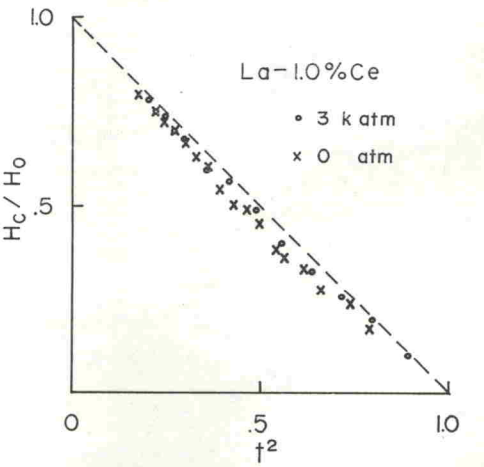

Fig. 6. Reduced critical field vs. reduced temperature of La−1.0% Ce.

§ 4. Conclusion

The pressure dependence of $N(0)$ of La was obtained from the measurement of thermodynamic critical field at high pressure. The large increase of $N(0)$ with pressure was interpreted as the increase of electronic population in the high density of states band such as d-band.

The increase of $N(0)$ cannot be explained with the contribution only from the 4f-like state just above the Fermi level. This conclusion is supported by the change of T_c and J with pressure of La-Ce alloy.

Acknowledgement

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