PHYSICAL REVIEW B VOLUME 58, NUMBER 6 1 AUGUST 1998-II

Impact of La substitution on the magnetic structure of a low-carrier-density Kondo system: $Ce_{0.9}La_{0.1}P$

M. Kubota, Y. Oohara, and H. Yoshizawa
Neutron Scattering Laboratory, I.S.S.P., University of Tokyo, Tokai, Ibaraki 319-1106, Japan

N. Mōri
I.S.S.P., University of Tokyo, Roppongi, Minato-ku, Tokyo 106-0032, Japan

H. Takahashi
College of Humanities and Sciences, Nihon University, Setagaya-ku, Tokyo 156, Japan

A. Uesawa and T. Suzuki
Department of Physics, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

(Received 5 January 1998)

We have performed neutron-diffraction measurements on $Ce_{0.9}La_{0.1}P$ under high pressure. The La-substituted $Ce_{0.9}La_{0.1}P$ system exhibits a P-T magnetic phase diagram very similar to that of the parent compound CeP. The large local randomness on the Ce lattice, however, introduces drastic changes in the magnetic structure of the La-substituted system. [S0163-1829(98)50430-4]

The Ce monopnictides CeX (X=P, As, Sb, Bi) are semimetals with extremely low carrier densities, typically ranging from 0.5% to 2.0%/Ce.[1] Among them CeP is particularly unusual; its resistivity shows a typical Kondo-type logarithmic behavior whereas the La-substituted system, $Ce_xLa_{1-x}P$ with $x=0.02$, exhibits normal metallic conductivity with no evidence of Kondo behavior.[2] This is in contrast to the behavior of a conventional heavy fermion system.[3]

The magnetic properties of CeX are also unusual. Despite its simple rock salt structure, CeX exhibits rich H-T and P-T phase diagrams involving complicated magnetic structures.[4,5] It has been reported, for example, that CeP exhibits a series of magnetic structures with mixed magnetic states.[6] In this system the $J=5/2$ multiplet of the Ce^{3+} ion splits into a twofold Γ_7 ground state and a fourfold excited Γ_8 state with a crystal-field splitting of 170 K.[7] Its magnetic structure consists of a stacking of (001) layers with long periodicity, in which ferromagnetically coupled double (001) layers ''↑↑'' with $2\mu_B$/Ce are separated by several paramagnetic (001) layers such as ''↑↑···↑↑''.[8] The double ferromagnetic layers are claimed to have a Γ_8 character because their moment is close to the moment of the Γ_8 state, $1.6\mu_B$/Ce. With decreasing temperature, the paramagnetic layers order antiferromagnetically with a magnetic moment of $\sim 0.8\mu_B$/Ce of the Γ_7 state.[6] [Hereafter, we refer to this kind of magnetic structure as a ''long period stacking'' (LPS) structure.]

In the early work of Kasuya and co-workers[9] they discussed the importance of the p-f mixing interaction between the holes with Γ_8 symmetry at the Γ point and the Γ_8 state of $4f$ electrons, and they successfully explained the sequence of magnetic structures observed in CeSb and CeBi.[5] By extending this theory, and by taking account of the extremely low density of carriers in the CeX system, Kasuya recently proposed the magnetic polaron (MP) model in order to explain the unusual transport and magnetic properties in CeP and CeAs.[10–12] Two important ingredients of the MP model to explain the aforementioned unusual LPS ordering are (1) the strong anisotropic p-f mixing interaction, and (2) the hole Wigner crystallization. The latter ingredient implies the phase separation between a hole-rich region (ferromagnetic layers) and a hole-poor region (paramagnetic layers). The strong anisotropic p-f mixing interaction favors the formation of the (001) ferromagnetic Γ_8 layers in the hole-rich region, and leads to the unusual coexistence of the Γ_8 and Γ_7 states in the LPS ordering. After the observation of the LPS ordering in CeP, on the other hand, Kasuya and co-workers[11] noted that its periodicity seems to be primarily determined by nesting effects of the Fermi surface. If this is the case, however, it may not be necessary to invoke the Wigner crystallization of holes in order to account for the LPS ordering in CeP.

At the present stage, the importance of the p-f mixing interaction is unquestionable, but the possibility of the hole crystallization in these systems is controversial. In fact, while the MP model seems to account for many aspects of the LPS ordering, to this date there are no reports of the experimental observation of magnetic polarons in these systems. It is of considerable importance then to elucidate the mechanism of the unusual phase separation between the hole-rich and hole-poor regions by experimentally examining the LPS ordering in CeP in more detail. Since the interaction of carriers with localized f electrons plays a crucial role, the substitution of Ce ions with La ions—which have no f electrons—provides unique information about the role of f electrons in the Ce monopnictides. The La substitution also causes negative chemical pressure and random local distortions of the lattice, which are expected to have strong effects on magnetic as well as transport properties of CeP. Since the number of nearest-neighbor sites in the rock salt

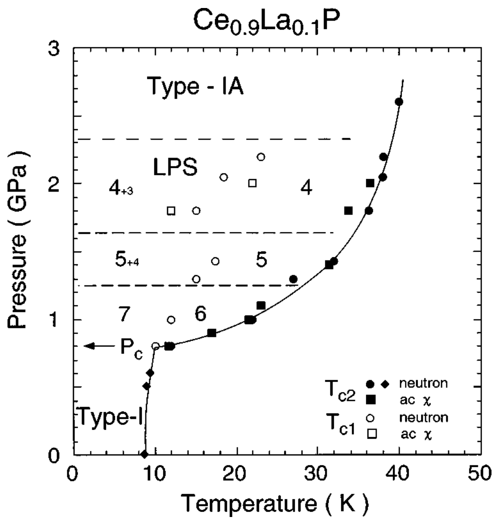

FIG. 1. P-T magnetic phase diagram for $Ce_{0.9}La_{0.1}P$. The numbers in the phase diagram denote the period of the LPS structures. The solid curves indicate the phase boundary between the paramagnetic and type-I antiferromagnetic phase below P_C and that between the paramagnetic and IM phase of the LPS ordering above P_C, respectively. The transition temperatures at T_{C2} and at T_{C1} are denoted by filled and open symbols, respectively.

structure is 12, we prepared La-substituted samples which contain 10% La ions so that at least one of the nearest-neighbor sites of Ce ions is occupied by a nonmagnetic La ion. If the LPS ordering were formed through the Wigner crystallization of holes as the MP model proposed, this ordering would be very sensitive to the local randomness and could be easily destroyed in the La-substituted system.

Neutron-diffraction studies were performed on the triple-axis spectrometer GPTAS at JRR-3M in JAERI. An incident neutron beam with a wave number of $k_i = 2.57$ Å^{-1} was obtained by the PG (002) reflection, and a double-axis mode with 40′-80′-80′ collimators was employed as the spectrometer configuration. The sample, a single crystal of $Ce_{0.9}La_{0.1}P$ of $3\times3\times3$ mm^3, and a NaCl single crystal used for pressure calibration were mounted on an aluminum sample holder which was placed in a piston-type pressure cell. A mixture of deuterated ethyl and methyl alcohol of a volume ratio of 4:1 was used as a pressure transmitting medium. The pressure cell was cooled by a closed-cycle He gas refrigerator.

Under high pressure the sample showed a severe inhomogeneity of domain distribution. While at ambient pressure there is an equal distribution of x, y, and z domains, the volume fraction of the x domain was 80% and 90% at 1.4 GPa and at 2.2 GPa, respectively. This illustrates the importance of considering of the domain distribution in the analysis of the magnetic structure. We have determined the volume fraction of the x domain by evaluating the integrated intensity of the (111) and (311) ferromagnetic reflections, and carried out the analysis of the magnetic structure by taking account of the inhomogeneous domain distribution as well as the extinction effect.

Figure 1 shows the P-T phase diagram of $Ce_{0.9}La_{0.1}P$. In the overall picture this phase diagram is very similar to that of CeP. Above the critical pressure $P_C \sim 0.8$ GPa, a ferromagnetic component appears in the magnetic structure. The

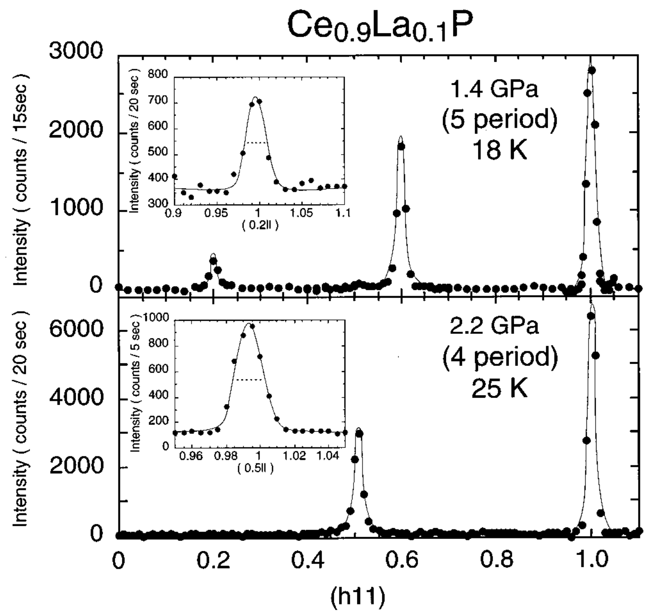

FIG. 2. Typical profiles for the LPS ordering in the IM phase at 1.4 and at 2.2 GPa. The curves shown are guides to the eye.

La substitution causes a negative pressure due to the larger radius of the La ion than that of the Ce ion, and this effect well explains the increase of P_C from $\sim$0.25 GPa for CeP to $\sim$0.8 GPa for $Ce_{0.9}La_{0.1}P$.[13] Below P_C, $Ce_{0.9}La_{0.1}P$ has the type-I antiferromagnetic structure "↑↓↑↓", where magnetic moments are ordered ferromagnetically within (100) planes in the x domain, and such ferromagnetic (100) sheets are stacked antiferromagnetically along the [100] direction.[8] Above P_C, on the other hand, the LPS magnetic ordering coexists with the ferromagnetic component, and its periodicity becomes shorter as the pressure is increased. Above $\sim$2.6 GPa, the magnetic structure converges to the type-IA structure "↑↑↓↓".

As a function of temperature, $Ce_{0.9}La_{0.1}P$ exhibits two ordered phases in the P-T phase diagram; the intermediate (IM) phase below T_{C2} and the low-temperature (LT) phase below T_{C1}. Note that we use the same notation of Ref. 6 for the two transition temperatures, T_{C2} and T_{C1}. We also performed ac susceptibility measurements in order to independently determine the transition temperature T_{C2}, and the results were in good agreement with those of neutron-diffraction measurements. Although a detailed characterization of the LT phase will be published elsewhere, we emphasize that the transition at T_{C1} in $Ce_{0.9}La_{0.1}P$ is strongly first order. This system exhibits distinct hysteresis upon entering the LT phase, and a few LPS structures coexist at low temperatures. The severe hysteresis prevented us from determining the phase boundary between the IM and LT phases. This should be compared with CeP where the transition to antiferromagnetic ordering on the Γ_7 cites at T_{C1} was reported to be close to second order, and the phase boundary T_{C1} is smooth and is almost parallel to the pressure axis.[6]

Figure 2 shows typical diffraction patterns along the (h11) direction at selected pressures. These scans provide information on the stacking of the ferromagnetic (100) layers along the [100] direction in the LPS ordering. These patterns indicate that the LPS ordering has a period of five layers and

TABLE I. Magnetic structure factors in the intermediate phase at 2.2 GPa at 25 K. Model I: magnetic polaron model ($S_1=S_2=2.0$, $S_3=S_4=0$); Model II: ferromagnetic double layer model ($S_1=S_2=1.2$, $S_3=S_4=0.17$); Model III: modulated structure model [$S_i=0.68+0.73\cos(\mathbf{q}\cdot\mathbf{r}_i)$].

		$\lvert\mathbf{F}_{mag}(hkl)\rvert^2_{cal}$		
(hkl)	$\lvert\mathbf{F}_{mag}(hkl)\rvert^2_{obs}$	Model I	Model II	Model III
(111)	29.9 (±8.3)	64	29.9	29.9
(0.511)	8.4 (±2.3)	32	8.4	8.4

four layers at 1.4 GPa and at 2.2 GPa, respectively. The insets in Fig. 2 show diffraction patterns along the in-plane direction of the (100) plane. Because the linewidths of the profiles perpendicular and parallel to the (100) plane are resolution limited, we can establish that the ordering in the IM phase is truly long-range order.

As mentioned above, a very unusual LPS order was reported to exist under high pressure in CeP. A similar long-range LPS magnetic ordering is observed in the La-substituted $Ce_{0.9}La_{0.1}P$ sample in the present study, indicating that the LPS ordering in CeP seems to survive the La substitution. In order to explore the influence of the La substitution on the LPS ordering, we have analyzed the magnetic structures in the IM phase of $Ce_{0.9}La_{0.1}P$. In Tables I and II we summarize the observed and calculated magnetic structure factors $|\mathbf{F}_{mag}(hkl)|^2_{obs}$ and $|\mathbf{F}_{mag}(hkl)|^2_{cal}$ for the ordering in the IM phase at 1.4 GPa and 2.2 GPa, respectively. In the table captions, $\{S_1,S_2,\ldots,S_n\}$ denote the magnetic moments in the magnetic unit cell of the LPS structure with a period of n spins. In these tables Model I corresponds to the magnetic structure reported for CeP; this model overestimates the observed intensities by more than a factor of 2. By allowing the variation of the size of the magnetic moments in Model I, but keeping the spin arrangement of the ferromagnetic double layers, we can easily find a solution which satisfactorily explains the observed intensities as shown in the columns labeled as Model II. By allowing a sinusoidal modulation of the moments (Model III) we can also explain the observed intensities equally well. Although we cannot determine a unique magnetic structure that is compatible with our diffraction experiment, we slightly favor Model III as a possible magnetic structure in the IM phase of $Ce_{0.9}La_{0.1}P$. This is because the temperature dependence of the relative ratio of the intensity of the peak at $h=0.2$ against

TABLE II. Magnetic structure factors in the intermediate phase at 1.4 GPa at 18 K. Model I: magnetic polaron model ($S_1=S_2=2.0$, $S_3=S_4=S_5=0$); Model II: ferromagnetic double layer model ($S_1=S_2=1.08$, $S_3=S_4=S_5=0.2$); Model III: modulated structure model [$S_i=0.55+0.53\cos(\mathbf{q}\cdot\mathbf{r}_i)+0.18\cos(2\mathbf{q}\cdot\mathbf{r}_i)$].

		$\lvert\mathbf{F}_{mag}(hkl)\rvert^2_{cal}$		
(hkl)	$\lvert\mathbf{F}_{mag}(hkl)\rvert^2_{obs}$	Model I	Model II	Model III
(111)	30.2 (±6.8)	64	30.2	29.9
(0.611)	8.1 (±1.6)	41.9	8.2	7.1
(0.211)	1.7 (±0.3)	6.1	1.2	0.8

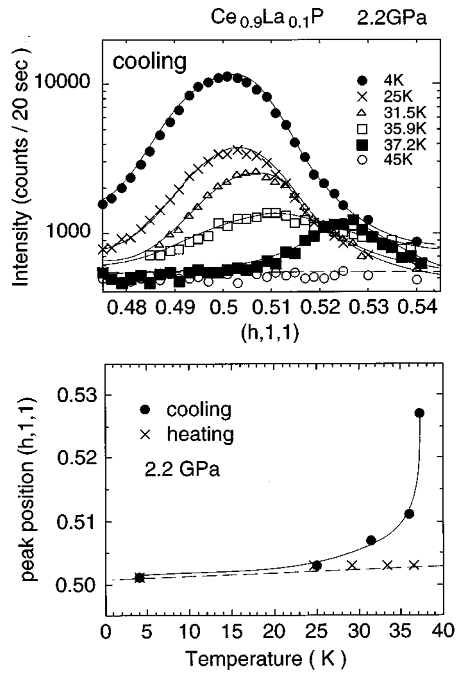

FIG. 3. Temperature dependence of the profile near $h\sim 1/2$ for the type-IA structure, and temperature dependence of the peak position.

that at $h=0.6$ shown in Fig. 2 indicates that the five-period LPS structure in the IM phase is close to a sinusoidal modulation, but it is strongly squared up in the LT phase.

It should be noted that the ferromagnetic double layer with $2\mu_B$/Ce does not appear in either of Models II or III. By evaluating the spin-correlation functions, we can further demonstrate that the consecutive paramagnetic layers of the CeP structure do not exist in the IM phase of $Ce_{0.9}La_{0.1}P$. We denote the spin-spin pair-correlation function for ferromagnetic layers with the distance $\boldsymbol{\delta}$ as $\langle \boldsymbol{S(0)\cdot S(\delta)}\rangle$. If there were consecutive paramagnetic layers, the strong condition that $\langle \boldsymbol{S(0)\cdot S(a)}\rangle\equiv 0$ would always hold for $\boldsymbol{\delta}=\boldsymbol{a}$, where $\boldsymbol{a}$ is a lattice constant. By evaluating the correlation functions for the LPS ordering with the four- and five-layer period, we obtained that $\langle \boldsymbol{S(0)\cdot S(a)}\rangle_4=0.20(\pm 0.11)$, and $\langle \boldsymbol{S(0)\cdot S(a)}\rangle_5=0.18(\pm 0.07)$, respectively. Since $\langle \boldsymbol{S(0)\cdot S(a)}\rangle\neq 0$ for both cases, we exclude the possibility of the consecutive paramagnetic layers in the IM phase of $Ce_{0.9}La_{0.1}P$. Clearly, these results demonstrate that the La substitution causes a drastic change of the actual spin arrangement in the LPS ordering in $Ce_{0.9}La_{0.1}P$.

A natural question one may ask is what determines the periodicity of the LPS ordering. According to the MP model, the LPS ordering is formed through the Wigner crystallization of holes. For the actually observed LPS ordering in CeP, on the other hand, the LPS ordering seems to be governed by nesting effects,[6,11] because its periodicity is either close to the diameter of the Fermi surface obtained by the band calculation,[11] or to the observed periodicity in the de Haas–van Alphen measurements.[6] An alternative approach that explicitly accounts for these effects, the Kondo semimetal model, was proposed by Ueda and co-workers.[14] This theory considers three factors: (I) competition between the intraband and the interband exchange interactions, (II) competition between the anisotropy and the exchange couplings, and

(III) commensurability which may stabilize the commensurate magnetic ordering through the gain of kinetic energy of the conduction electrons. In this model, the nesting effects of Fermi surfaces essentially determine the periodicity of the LPS structure, and even a simplified one-dimensional version can qualitatively reproduce features of the observed phase diagram.[14]

If the competition between the nesting effects and the commensurability is a major driving force for the LPS ordering, it should be possible to continuously change the LPS periodicity in a real material. We observed such a continuous change in the periodicity of the type-IA ordering at 2.2 GPa as shown in Fig. 3. At T_{C2}, the magnetic superlattice peak appears at the incommensurate position. With decreasing temperature, it quickly shifts and is locked in at the commensurate position $h=1/2$. In the heating process, however, the peak position is completely locked. This result is a clear manifestation of the competition between the Fermi-surface nesting effect and the commensurability effect. Considering all available experimental results and existing theories, we conclude that the p-f mixing interaction and the Fermi-surface nesting effect are two indispensable ingredients to account for the unusual LPS ordering in CeP and $Ce_{0.9}La_{0.1}P$, but the precise mechanism of the formation of the LPS ordering and especially the origin of the ferromagnetic double layer in the parent material CeP should be further examined. We also note that the LPS ordering itself is not a direct evidence of the existence of the magnetic polarons in CeP.

In conclusion, we have demonstrated that, despite similarities of the P-T phase diagrams of pure CeP and the La-substituted system, the La substitution causes drastic differences in the magnetic structure. A detailed analysis revealed that the La-substituted $Ce_{0.9}La_{0.1}P$ sample does not exhibit the consecutive paramagnetic layers observed in the ordered phase of the pure system, and that the magnetic moments at all sites do not exceed the value of the saturated moment of the Γ_8 state, $1.6\mu_B$/Ce. These results indicate that the magnetic ordering in $Ce_{0.9}La_{0.1}P$ is rather conventional, although the total moment certainly increases over the Γ_7 value for $P>P_c$.

We thank Dr. J. A. Fernandez-Baca for a critical reading of the manuscript.

[1] Y. Haga, A. Uesawa, Y. S. Kwon, T. Suzuki, T. Terashima, S. Uji, and H. Aoki, Physica B **206&207**, 792 (1995); N. Takeda, Y. S. Kwon, Y. Haga, N. Sato, T. Suzuki, and T. Komatsubara, *ibid.* **186-188**, 153 (1993); R. Settai, T. Goto, S. Sakatsume, Y. S. Kwon, T. Suzuki, Y. Kaneta, and O. Sakai, J. Phys. Soc. Jpn. **63**, 3026 (1994).

[2] Y. Haga, Y. S. Kwon, T. Suzuki, and T. Kasuya, Physica B **199&200**, 525 (1994); T. Kasuya and Y. Haga, Solid State Commun. **93**, 307 (1995).

[3] For a typical crossover from dense- to dilute impurity-Kondo behavior, see, for example, A. Sumiyama, Y. Oda, H. Nagano, Y. Onuki, K. Shibutani, and T. Komatsubara, J. Phys. Soc. Jpn. **55**, 1294 (1986).

[4] For a review, see T. Kasuya, Jpn. J. Appl. Phys. Series **8**, 3 (1993); T. Suzuki, *ibid.* **8**, 267 (1993); T. Kasuya, Physica B **186-188**, 9 (1993); T. Suzuki, *ibid.* **186-188**, 347 (1993), and references cited therein.

[5] J. Rossat-Mignod, P. Burlet, S. Quezel, J. M. Effantin, D. Delacôtte, H. Bartholin, O. Vogt, and D. Ravot, J. Magn. Magn. Mater. **31-34**, 398 (1983); **52**, 111 (1985); T. Chattopadhyay, P. Burlet, J. Rossat-Mignod, H. Bartholin, C. Vettier, and O. Vogt, Phys. Rev. B **49**, 15 096 (1994), and references cited therein.

[6] M. Kohgi, T. Osakabe, K. Iwasa, J. M. Mignot, I. N. Goncharenko, Y. Okayama, H. Takahashi, N. Mōri, Y. Haga, and T. Suzuki, J. Phys. Soc. Jpn. **65** Suppl. B, 99 (1996); T. Osakabe, M. Kohgi, K. Iwasa, N. Nakajima, J. M. Mignot, I. N. Goncharenko, Y. Okayama, H. Takahashi, N. Mōri, Y. Haga, and T. Suzuki, Physica B **230-232**, 645 (1997).

[7] H. Yoshizawa, Y. Okayama, Y. Oohara, H. Takahashi, N. Mōri, S. Mitsuda, T. Osakabe, M. Kohgi, Y. Haga, and T. Suzuki, J. Phys. Soc. Jpn. **64**, 617 (1995).

[8] The cubic symmetry allows stacking along the [100] and [010] directions, forming three equivalent magnetic domains.

[9] H. Takahashi and T. Kasuya, J. Phys. C **18**, 2697 (1985); **18**, 2709 (1985); **18**, 2721 (1985); **18**, 2731 (1985); **18**, 2745 (1985); **18**, 2755 (1985).

[10] T. Kasuya *et al.*, J. Phys. Soc. Jpn. **61**, 2206 (1992); **61**, 2628 (1992); **61**, 3447 (1992).

[11] T. Kasuya *et al.*, J. Phys. Soc. Jpn. **62**, 411 (1993); **62**, 2549 (1993); **62**, 3376 (1993).

[12] T. Kasuya, J. Phys. Soc. Jpn. **63**, 4318 (1994); **64**, 1453 (1995).

[13] N. Mōri, Y. Okayama, H. Takahashi, Y. Haga, and T. Suzuki, Physica B **186-188**, 444 (1993).

[14] K. Ueda, N. Shibata, and C. Ishii, Physica B **223&224**, 426 (1996); N. Shibata, C. Ishii, and K. Ueda, Phys. Rev. B **52**, 10 232 (1995).