

Magnetocrystalline Anisotropy of Magnetic Dense-Kondo Compound CePdAl

Y. ISIKAWA, T. MIZUSHIMA, N. FUKUSHIMA, T. KUWAI,
J. SAKURAI and H. KITAZAWA¹

Department of Physics, Toyama University, Toyama 930, Japan

¹*National Research Institute for Metals, Tsukuba 305, Japan*

Intermetallic compound CePdAl, which crystallizes in the hexagonal ZrNiAl-type structure, is a dense-Kondo compound with a magnetic transition temperature $T_N = 2.9$ K. The temperature dependence of the magnetization, magnetic susceptibility and electrical resistivity have been measured by using single crystalline samples prepared by the Czochralski method. The easy direction of magnetization is parallel to the c -axis. The metamagnetic feature is observed by applying the magnetic external field parallel to the c -axis below T_N . The energy scheme of Ce ions is tentatively deduced by analyzing the temperature dependence of magnetic susceptibility taking into account of both the crystalline electric field and anisotropic exchange field.

KEYWORDS: CePdAl, magnetic anisotropy, crystal electrical field, heavy fermion

§1. Introduction

Intermetallic compound CePdAl was found to be a new antiferromagnetically ordered heavy-fermion compound ($T_N=2.7$ K) by Kitazawa *et al.*¹⁾ The electrical resistivity as a function of temperature was found to show characteristic behaviors of the magnetic dense-Kondo compounds; the minimum around 20K, $-\ln T$ dependence, a broad maximum at 4 K, and a steep decreases below T_N of about 3K. These behaviors are smeared by applying a magnetic field, and the $-\ln T$ dependence nearly disappears at 14 T.

The λ -type specific heat anomaly^{1,2)} appears at 2.7K, which we take as T_N . The electronic specific-heat coefficient γ_0 is 270 mJ/K²-mol, showing a feature of an *intermediate* heavy-fermion. A tail of the λ -type specific heat of this compound extends to considerably higher temperatures. Thus, the magnetic entropy S_{mag} per mole at T_N is only 38% of $R \ln 2$. If we do not carry out the subtraction of the phonon and electron contributions, the total entropy S at T_N is 55 % of $R \ln 2$. The total entropy S exceeds $R \ln 2$ at about 8K. This reduction of S may be due not only to a large magnetic short-range order above T_N , but also to the Kondo effect. This is one of the interesting points of this compound.

Very recently, the specific-heat measurement under pressure has been carried out by Tang *et al.*,³⁾ and the T_N is found to be greatly suppressed down to 1.7 K under 0.9 GPa. Thus it is expected that a chemical pressure effect by substituting Pd atoms with Ni ones is also substantial.

The magnetic susceptibility⁴⁾ obeys the Curie-Weiss law with an effective moment of $2.49\mu_B$ and the paramagnetic Curie temperature Θ_p of 5K above 150 K. At lower temperatures the inverse magnetic susceptibility deviates from the Curie-Weiss law. A discontinuous increase in the slope is observed in the magnetization curve between 1.4 and 5.5 T at 1.6 K and the value of the magnetization is

saturated towards $1.2\mu_B$ at 10 T. Magnetic structure has been studied by neutron powder-diffraction experiments using polycrystalline sample, from which an incommensurate structure⁵⁾ has been inferred.

The crystal structure⁶⁾ of CePdAl is the hexagonal ZrNiAl-type, which is an ordered Fe₂P-type derivative. The space group is $P\bar{6}2m$ (No.189) with 3f site occupied by Ce atoms, 1a and 2d sites by Pd atoms and 3g site by Al atoms. This crystal structure is observed as a high-temperature phase by the investigation by Schank *et al.*²⁾ They had shown that (1) after an annealing at temperatures between 700 °C and 900 °C, the X-ray diffraction pattern indicates a structural phase transition or chemical decomposition and (2) an annealing process at 1000 °C leaves the original X-ray pattern almost unchanged. As pointed out by Schank *et al.*, the as-cast sample contains typically about 10 % of a foreign phase and it has been difficult to prepare good-quality crystals of CePdAl. Since the crystalline magnetic anisotropy is expected to be large due to the hexagonal symmetry, a growth of single crystals has been desired.

In this paper, we report that the single-crystal CePdAl have been successfully grown, and we present the anisotropic properties of the electrical resistivity and magnetic susceptibility of CePdAl. The anisotropic magnetic susceptibility will be analyzed numerically taking into account of the crystal-field effect and the exchange interaction. Lastly the chemical pressure effect by replacing Pd atoms to Ni atoms will be presented.

§2. Experimental Procedure

The single crystal of CePdAl was grown by the Czochralski method in an argon gas atmosphere of 5 torr using a tungsten crucible in an induction furnace. The purities of the starting materials were 99.9 % for Ce and Pd and 99.999 % for Al. The pulling speed was 10 mm/hour

with the rotation speed of 5 rpm. Part of the single crystal was pulverized for the X-ray powder-diffraction measurement, which confirmed the hexagonal ZrNiAl-type structure with an existence of a few percents contamination of a foreign phase. Annealing of this sample was not done for the present experiment. The crystal directions were determined by the X-ray back-Laue reflection technique. The sample with a shape of a cube of 2.3 mm^3 is cut for the magnetization measurement and the samples with a shape of rectangles parallel to the a-axis and the c-axis are cut for the electrical-resistivity measurement. Magnetic measurement was carried out using a vibration-sample magnetometer (VSM) in the temperature range between 1.6 and 300 K under the magnetic fields up to 7.5 T applied by a superconducting magnet. Electrical resistivity was measured by a conventional four-probe DC method in the same temperature range.

The samples of polycrystalline $\text{CePd}_{1-x}\text{Ni}_x\text{Al}$ were prepared by arc-melting in an argon gas atmosphere. The X-ray powder diffraction pattern confirmed that the samples crystallize in the same ZrNiAl-type hexagonal structure in the entire region of Ni concentration x with a contamination of a few percents of a foreign phase.

§3. Experimental Results

3.1 Electrical resistivity of CePdAl

Fig. 1(a) shows the temperature dependence of the electrical resistivity, ρ_a and ρ_c , along the a- and c-axes, respectively. Fig. 1(b) shows ρ vs. $\ln T$. The linearity of ρ to $-\ln T$, the characteristic behavior of Kondo compounds, is apparently observed between 5 and 18 K for both the a- and c-axes. The maximum around 4 K is speculated to be an onset of the Kondo-lattice formation. The resistivity decreases steeply below $T_N \sim 3 \text{ K}$. The anisotropy of ρ is very large but the temperature dependence qualitatively shows the similar behavior for each axis. The value of ρ_c is about 7 times larger than that of ρ_a in the whole temperature range. Comparing with the data of the polycrystalline samples¹⁾, the value of ρ_a is smaller by an approximate factor of 1/20. Qualitatively all curves of ρ vs. T for the single crystals along the a- and c-axes and polycrystal samples show the same behaviors. However the value of ρ at 1.8 K is large, which may be due to the cracks in the samples.

3.2 Magnetic Properties of CePdAl

Fig. 2 shows the temperature dependence of the magnetic susceptibility, χ_a and χ_c along the a- and c-axis, respectively. Fig. 3 shows the magnetic susceptibility in an enlarged scale in the low temperature region. The Néel temperature, T_N , is about 2.9 K, which is in agreement with the polycrystalline data^{1,2,4)}. The value of χ_c at T_N is about 14 times greater than that of χ_a . The χ_c decreases sharply below T_N with decreasing the temperature, on the other hand, the χ_a becomes constant. It is suggested from these observations that a magnetic structure of CePdAl is antiferromagnetic with the magnetic moments aligned parallel to the c axis.

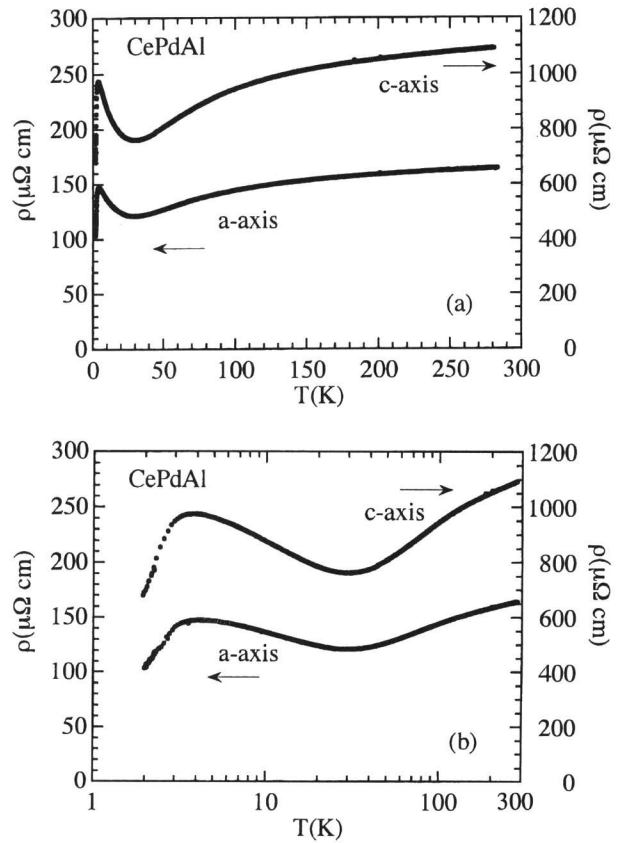


Fig. 1. The temperature dependence of the electrical resistivity ρ of the single-crystal CePdAl for the a- and c-axes. (a) ρ vs. T , (b) ρ vs. $\ln T$.

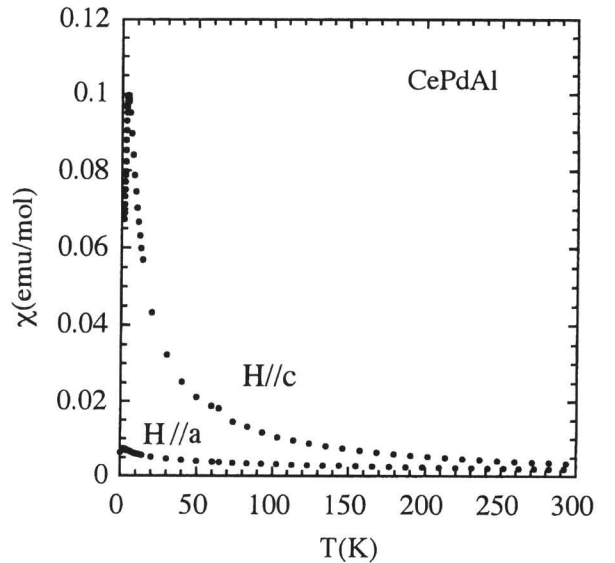


Fig. 2. The temperature dependence of the magnetic susceptibility of the single-crystal CePdAl in the magnetic fields parallel to the a- and c-axis.

Fig. 4 shows the temperature dependence of the inverse magnetic susceptibility, $1/\chi$, which obeys the Curie-Weiss law between 150 and 300 K. The effective Bohr magneton, μ_{eff} , and the paramagnetic Curie temperature, Θ_p , are $2.71 \mu_B$ and -181 K for the a-axis, and $2.69 \mu_B$ and $+30 \text{ K}$ for

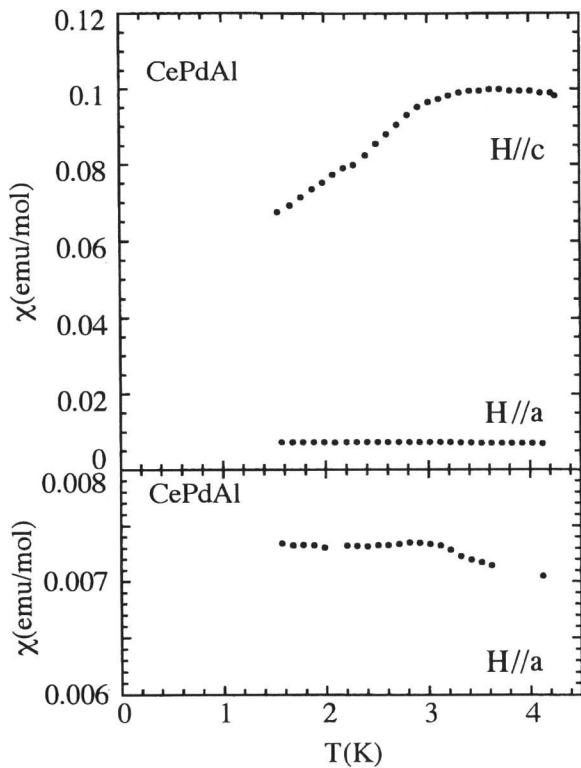


Fig. 3. The temperature dependence of the magnetic susceptibility of the single-crystal CePdAl. (enlarged one in low temperatures)

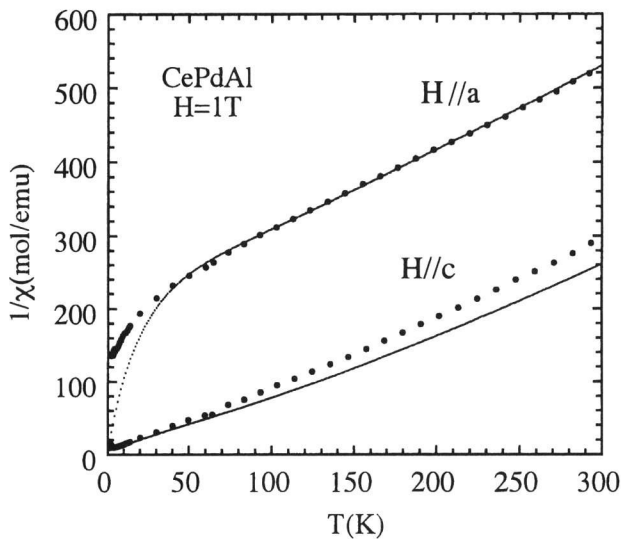


Fig. 4. The temperature dependence of the inverse magnetic susceptibility of the single-crystal CePdAl in the magnetic fields parallel to the a- and c-axis. Thin lines are the calculated ones. See text.

the c-axis, respectively. It is considered that such extreme large value of the negative Θ_p for the a-axis reflects the Kondo effect. The value of Θ_p estimated for the polycrystalline sample⁴⁾ was positive. Moreover p_{eff} differs from the value of the free cerium ions. The temperature dependence of this anisotropic $1/\chi$ will be analyzed later taking into account of the crystal-electric-field effect and the

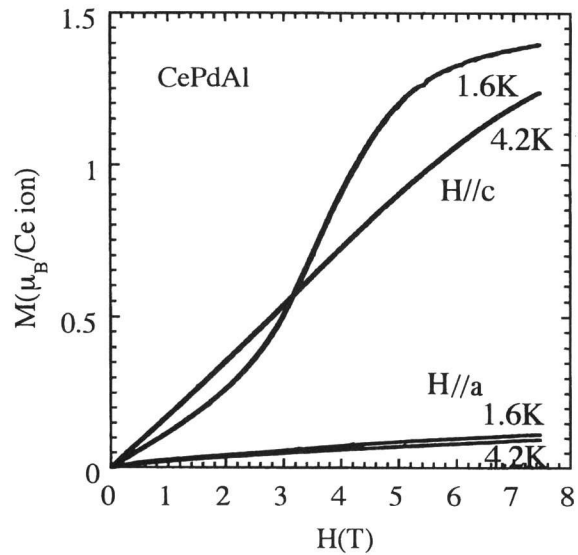


Fig. 5. Magnetization curves of the single-crystal CePdAl at 1.6 and 4.2 K in the fields parallel to the a- and c-axis.

anisotropic exchange interaction.

Fig. 5 shows the magnetization curves at 1.6 and 4.2 K in the magnetic fields up to 7.5 T along the a- and c-axes, respectively. The metamagnetic behavior has been observed at 1.6 K in the magnetic fields parallel to the c-axis. The slope of this metamagnetic transition between 3 and 4 T is $0.42 \mu_B/T$. Assuming that the demagnetization factor N is $-4\pi/3$ in the cgs unit, the slope of the first-order transition must be $16 \mu_B/T$. However, the experimental slope of the metamagnetic transition is extremely small comparing to the slope due to the demagnetization field. Thus it is found that the transition is not originated from the spin-flip as normally observed in a simple antiferromagnetic compound. This metamagnetic behavior is supposed to be due to a sequential change of complex magnetic structures although the magnetic structures under magnetic fields are not known at present time. The magnetization along the c-axis tends to be saturated towards $1.5 \mu_B$ in higher fields. The ratio of the magnetization along the c- and a-axes is 14 at 1.6 K in the field of 7.5 T. The strong magnetic anisotropy makes this compound CePdAl to be an Ising-type antiferromagnet.

3.3 Electrical resistivity of CePd_{1-x}Ni_xAl

Fig. 6(a) shows the ρ vs. T of the polycrystalline samples of CePd_{1-x}Ni_xAl. Fig. 6(b) shows the ρ vs. $\ln T$. The resistivity of polycrystalline CePdAl is 2 times and 20 times larger than those for the c- and a-axes of the single-crystal CePdAl, respectively. But the behaviors of temperature dependence are qualitatively the same as each other. High resistivity for the polycrystalline samples is probably caused by cracks, as mentioned by Kitazawa *et al.*¹⁾ In the sample of $x=0.2$ the $-\ln T$ dependence remains and the broad maximum can be seen around 13 K. But the $-\ln T$ dependence disappears completely in the samples of x larger than 0.4 as far as the data are limited below 300 K.

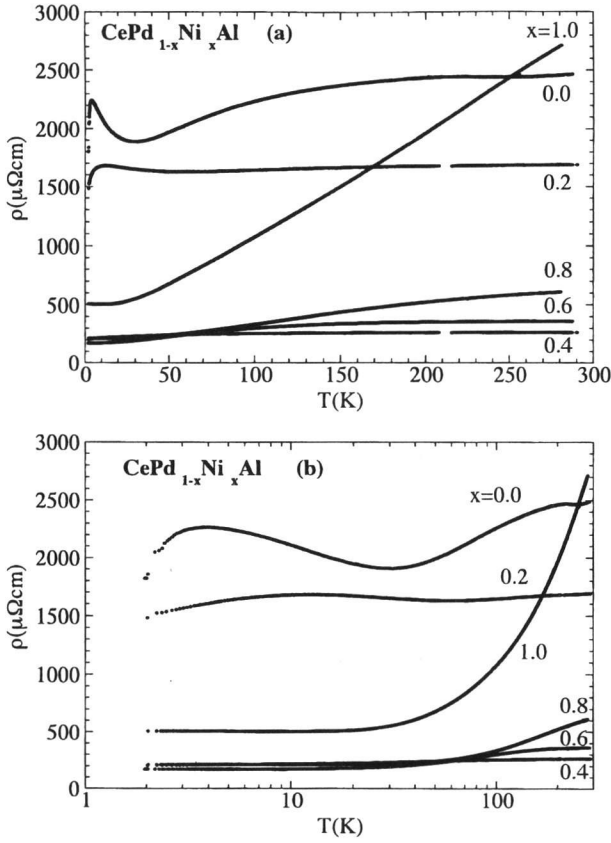


Fig. 6. The temperature dependence of the electrical resistivity ρ of polycrystalline $\text{CePd}_{1-x}\text{Ni}_x\text{Al}$. (a) ρ vs. T , (b) ρ vs. $\ln T$.

§4. Analysis and Discussion

4.1 Crystal-electric-field effect and exchange-field parameters

The anisotropic susceptibility of CePdAl is analyzed by the following crystal-electric-field (CEF) Hamiltonian

$$H_{\text{cry}} = \sum_{k,m} B_{km} C_{km}, \quad (1)$$

where B_{km} are the crystal-field parameters and C_{km} the irreducible spherical tensors.⁷⁾ The point symmetry at Ce atoms occupying on the 3f site is $m2m$, leading the point group C_{2v} . Because of the lack of the six-fold rotation symmetry at the site of Ce atoms, B_{km} with $m=\pm 2$ and ± 4 are not zero. Independent non-vanishing B_{km} are, therefore, $B_{20}, B_{2\pm 2}, B_{40}, B_{4\pm 2}$ and $B_{4\pm 4}$. It is noted that the x and y axes for symmetry operations are different for three Ce atoms at three different 3f sites as shown in Fig. 7, while the z axis for the three Ce atoms is the same and parallel to the c -axis. Thus, we have to consider three magnetic sublattices.

We next consider the exchange interaction between Ce atoms in the frame of the molecular-field approximation. In the case of the external field H^z parallel to the c -axis, the magnetization, M_1^z , M_2^z and M_3^z at each three magnetic sublattices induced by H^z and the molecular field are written

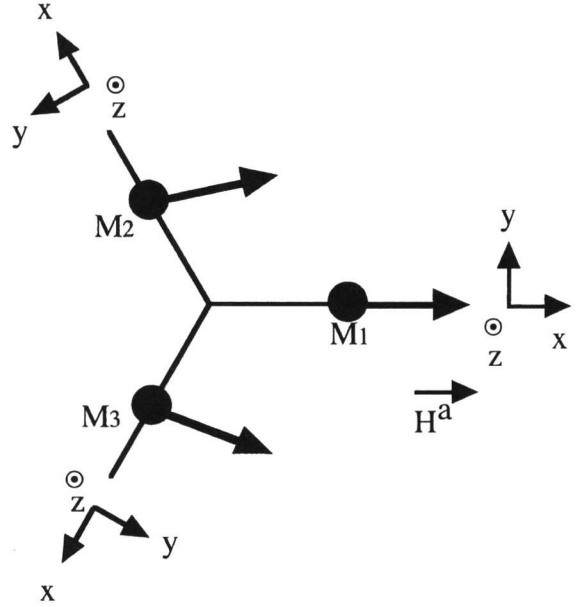


Fig. 7. Magnetic moments occupied in the three different magnetic sublattices. The arrays on the magnetic moments denote the moment directions when the external field is applied parallel to the a -axis.

$$\begin{aligned} M_1^z &= \chi_0^z \left\{ H^z - (\lambda_0^z M_1^z + \lambda_1^z M_2^z + \lambda_1^z M_3^z) \right\}, \\ M_2^z &= \chi_0^z \left\{ H^z - (\lambda_1^z M_1^z + \lambda_0^z M_2^z + \lambda_1^z M_3^z) \right\}, \\ M_3^z &= \chi_0^z \left\{ H^z - (\lambda_1^z M_1^z + \lambda_1^z M_2^z + \lambda_0^z M_3^z) \right\}, \end{aligned} \quad (2)$$

where λ_0^z and λ_1^z are constants of the molecular field and χ_0^z magnetic susceptibility calculated from CEF. From the total magnetization $M^z = (M_1^z + M_2^z + M_3^z)/3$, the inverse magnetic susceptibility $1/\chi^z$ is easily derived

$$\frac{1}{\chi^z} = \frac{1}{\chi_0^z} + \lambda^z, \quad (3)$$

where $\lambda^z = \lambda_0^z + 2\lambda_1^z$. In the case of the external field parallel to one special a -axis, H^a , we have to consider that the a -axis is not the principal axes for the other magnetic moments at the second and third 3f sites, as shown in Fig. 7. Consequently, each magnetization M_1^a , M_2^a and M_3^a are written

$$\begin{aligned} M_1^a &= \chi_0^x \left\{ H^a - (\lambda_0^a M_1^a + \lambda_1^a M_2^a + \lambda_1^a M_3^a) \right\}, \\ M_2^a &= \left(\frac{1}{4} \chi_0^x + \frac{3}{4} \chi_0^y \right) \left\{ H^a - (\lambda_1^a M_1^a + \lambda_0^a M_2^a + \lambda_1^a M_3^a) \right\}, \\ M_3^a &= \left(\frac{1}{4} \chi_0^x + \frac{3}{4} \chi_0^y \right) \left\{ H^a - (\lambda_1^a M_1^a + \lambda_1^a M_2^a + \lambda_0^a M_3^a) \right\}, \end{aligned} \quad (4)$$

where λ_1^a and λ_1^a are constants, and χ_0^x and χ_0^y are also calculated from CEF. The total magnetization along the a -axis is written,

Table I. CEF parameters, exchange field parameters, and the first and second excited energy.

	B20(K)	B2+2(K)	B40(K)	B4+2(K)	B4+4(K)	λz	λx	$\Delta 1(K)$	$\Delta 2(K)$
set 1	964	674	0	0	0	5.8	5.8	274	704
set 2	519	405	0	0	0	5.8	97	147	400
set 3	475	416	110	-290	58	5.8	97	169	409

$$M^a = \frac{\{A + 2B + 3AB(\lambda_0^a - \lambda_1^a)\}H^a / 3}{1 + A\lambda_0^a + B(\lambda_0^a + \lambda_1^a) + AB\left\{(\lambda_0^a)^2 + \lambda_0^a\lambda_1^a - 2(\lambda_1^a)^2\right\}}, \quad (5)$$

where $A = \chi_0^x$, $B = \frac{1}{4}\chi_0^x + \frac{3}{4}\chi_0^y$. When λ_0^a is equal to λ_1^a , the inverse magnetic susceptibility $1/\chi^a$ is expressed as

$$\frac{1}{\chi^a} = \frac{2}{(\chi_0^x + \chi_0^y)} + \lambda^a, \quad (6)$$

where $\lambda^a = 3\lambda_0^a$.

In order to interpret our experimental data, five B_{km} 's are treated as variable parameters in a least-squares fit. As a first step, we assumed that the terms of B_{km} with $k=4$ equal to zero and that the exchange interaction was isotropic; $\lambda z = \lambda^a$. The parameter λz was fixed to 5.5 mol/emu, to which the value of $1/\chi^z$ was extrapolated to 0K. The result is shown in Fig. 4 by small dots. The parameters used are listed in the set 1 of Table I. Experimentally the extrapolated value of $1/\chi^z$ to 0K is apparently different from that of $1/\chi^a$ to 0K, which value is 97 mol/emu. These values mean that the exchange interaction is anisotropic. Then, we supposed anisotropic molecular-field parameters and fixed the values of λz and λ^a separately to these extrapolated values. The result of the second step is listed in the set 2 of Table I. Finally we used all B_{km} as variable parameters and the result is listed in the set 3 of Table I. The temperature dependence of the calculated $1/\chi$ based on the set 3 is shown in Fig. 8 by small dots. The fitting to the experimental points was improved very well. The energy scheme, constructed by the three Kramers' doublets, are calculated from the CEF Hamiltonian using B_{km} parameters obtained in each fitting process. The first and the second excited energy, $\Delta 1$ and $\Delta 2$, are listed in Table I for each step. They are almost the same for the parameters in the sets 2 and 3. Hence, we would like to conclude that $\Delta 1$ and $\Delta 2$ are about 170 K and 410 K, respectively.

The mechanism of the anisotropic exchange interaction is not clear at present time. The energy scheme deduced by the present experiment of χ will be compared to the preliminary experimental results of specific heat up to 80K and inelastic neutron scattering. In the specific heat measurements up to 80, the Schottky-like anomaly was observed at around 45 K. It means that the energy splitting

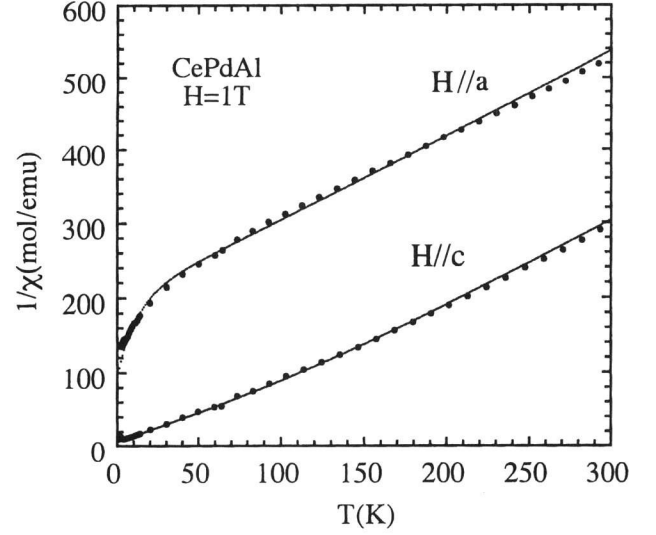


Fig. 8. The temperature dependence of the inverse magnetic susceptibility of the single-crystal CePdAl in the magnetic fields parallel to the a- and c-axis. Thin lines are the calculated ones. See text.

due to the CEF effect between the ground state and the first excited state is about 100 K. Very recently, inelastic neutron scattering experiments have been performed by using polycrystalline samples at 10 K.¹⁰⁾ Only one excitation was observed at about 24 meV. It may be caused by the CEF effect. Further information of inelastic neutron scattering and specific-heat measurements will be desired to check our tentative CEF energy scheme.

4.2 Substitution effect by Ni; $CePd_{1-x}Ni_xAl$

By replacing partially the Pd atoms by Ni atoms, we can expect the chemical pressure effect of this system because the ionic radius of Ni atom is less than that of Pd atoms. It is known⁸⁾ that CeNiAl exhibits a temperature-independent magnetic susceptibility, indicating that the Ce ion is in tetravalent state. It is also known⁸⁾ that the magnetization is altered by hydrogenation such that the susceptibility becomes temperature-dependent and obeys the Curie's law. The hydrogenation is equivalent to a negative pressure effect to expand the lattice spacing. The crystal structure of CeNiAl is the same as that of CePdAl. Then it is expected that the crossover from trivalent to tetravalent state of Ce ions would be observed.

Fig. 9 shows the lattice constant of the a- and c-axes of the solid solution of the two compounds against the

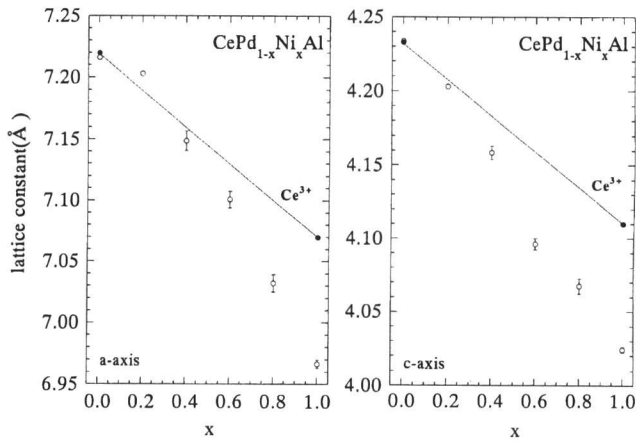


Fig. 9. The lattice constant of a- and c-axes of $\text{CePd}_{1-x}\text{Ni}_x\text{Al}$ against x .

concentration of Ni atoms, x . The filled points at $x=0$ are the data referred from the literature⁶⁾, and the filled points at $x=1$ are lattice constants estimated on the assumption that the valence of Ce in CeNiAl would be trivalent.⁹⁾ The lattice constant in RNiAl , where R denotes rare earth element, reduces smoothly with changing R from La to Sm if the Ce ion in CeNiAl is in the trivalent state. The lines in the figure, then, should show the Vegard's law on the assumption that the trivalent state of Ce does not change in $\text{CePd}_{1-x}\text{Ni}_x\text{Al}$. Experimentally the data points deviate from this line in the region of x larger than 0.4, which is indicating that the 4f state of Ce ions in $\text{CePd}_{1-x}\text{Ni}_x\text{Al}$ changes from trivalent to tetravalent state with increasing the Ni concentration. Then it is found that the $\text{CePd}_{1-x}\text{Ni}_x\text{Al}$ with x larger than 0.4 belongs to the valence-fluctuation regime. This change corresponds to the tendency of the x dependence of the electrical resistivity mentioned in §3.3.

§5. Summary

The electrical resistivity and the magnetic susceptibility

have been measured using the single crystalline samples of CePdAl . Strong magnetic anisotropy makes this compound to be an Ising-type antiferromagnet with the magnetic moments parallel to the c-axis. The anisotropy of the magnetic susceptibility had been analyzed sufficiently well by using four CEF and two anisotropic exchange parameters (λ^z, λ^a) in the temperature range above about 20 K. This means that the moment of Ce ions remains at the trivalent state in the paramagnetic state above 20 K. The energy scheme was tentatively deduced from the CEF parameters. The Kondo effect may be reflected by abnormally large λ^a . The mechanism of the anisotropic exchange interaction is not clear at present time.

- 1) H. Kitazawa, A.Matsushita, T.Matsumoto and T.Suzuki: *Physica B* **199&200** (1994) 28.
- 2) C.Schank, F.Jährling, L.Luo, A.Grauel, C.Wassilew, R.Borth, G.Olesch, C.D.Bredl, C.Geibel and F.Steglich: *J. Alloys and Compounds* **207/208** (1994) 329.
- 3) J.Tang, A.Matsushita, H.Kitazawa and T.Matsumoto: *Physica B* **217** (1996) 97.
- 4) F.Hulliger: *J. Alloys and Compounds* **196** (1993) 225.
- 5) A.Dönni, G.Ehlers, H.Maletta, P.Fischer, H.Kitazawa and M.Zolliker: to be submitted to *J. Phys.:Condens. Matt.*
- 6) B.Xue, H.Schwer and F.Hulliger: *Acta Cryst.* **C50** (1994) 338.
- 7) C.A.Morrison and R.P.Leavitt: *Handbook on the Physics and Chemistry of Rare Earth*, edited by K.A.Gschneidner, Jr and L.Eyring, vol. **5** (North-Holland publishing co., 1982) p461.
- 8) B.Bandyopadhyay, K.Ghoshray, A.Ghoshray, N.Chatterjee: *Phys. Rev.* **B38** (1988) 8455.
- 9) N.C.Tuan: *J. Appl. Phys.* **73** (1993) 5677.
- 10) A.Dönni *et al.*: private communication.