Separation of the 4*f*-spin, 4*f*-orbital, and conduction-electron magnetization from exotic thermomagnetic behavior for ferromagnetic Sm intermetallics

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The thermomagnetic curves of the ferromagnetic Sm intermetallics, polycrystalline samples of the CsCl-type compounds SmZn and SmCd, and a single crystal of the cubic Laves phase compound SmAl$_2$, have been measured in a temperature range from 2 to 300 K, and the exotic behavior has been well explained with the model of Sm^{3+} in a metallic matrix. The M-T curves in the ordered states for these compounds, just like those of ferrimagnets, reflect the different temperature dependences of the spin moment and the orbital one, which is due mainly to the thermal variation of the admixture among the J multiplets of the 4f electrons through the exchange field. Utilizing this property, the separation of the 4f-spin, 4f-orbital, and conduction-electron component from the total ordered moment has been successfully done. Some microscopic properties of these compounds, such as the difference between the conduction-electron polarization effect in the ordered state and that in the paramagnetic one, have been also suggested through the analysis. [S0163-1829(99)03117-3]

I. INTRODUCTION

The spin and the orbital parts of the ordered moment of Sm^{3+} have different temperature dependences due mainly to the thermal variation of the admixture among the 4f J multiplets through the exchange field. Since they ordinarily couple antiparallel, having almost the same magnitude, the difference could be remarkably reflected in the temperature dependence of the total ordered moment.[1] The size of each part is, furthermore, usually modified by the local environment surrounding the ion, and then the temperature dependence of the total moment is to be very different from substance to substance. This unique property of the Sm^{3+} ion also implies that, for the ferromagnetic intermetallics of Sm^{3+} with nonmagnetic ions, the possible variety of the thermomagnetic behavior would enable us to separate the partial magnetizations associated with the 4f-spin, 4f-orbital, and conduction-electron moment from the resultant one, through the analysis evaluating the effects of the crystal fields, the exchange interaction, and the conduction-electron polarization.

We have studied the thermomagnetic curves of ferromagnetic compounds SmZn, SmCd, and SmAl$_2$, where the cubic symmetry of the crystal fields acting on the Sm^{3+}ion is expected to make the analysis simpler. Some magnetic data on these compounds have been published so far,[2–9] but satisfactory explanations on their temperature dependences have not yet been given. In this paper, the results of the magnetic measurements in a temperature range from 2 to 300 K are quantitatively interpreted with the model of Sm^{3+} in a me-

tallic matrix, and the evaluation of each component forming the total moment is demonstrated. Some values of the parameters obtained by the analysis are also discussed.

II. EXPERIMENTAL

Polycrystalline samples of SmZn and SmCd were prepared by the induction melting of stoichiometric amounts in sealed quartz tubes with an argon or a helium gas. The reactants were then sealed again in quartz tubes at a reduced pressure of an inert gas and annealed at 600 °C for 2 days. The x-ray-diffraction patterns indicated that the samples thus obtained were of single phase with the lattice constants of 3.64 and 3.795 Å for SmZn and SmCd, respectively.

For SmAl$_2$, a single crystal was obtained by the Bridgeman method using a sealed tungsten crucible. The starting material used was the polycrystalline ingot, which was prepared in advance by argon-arc melting. By x-ray diffraction on the pulverized sample, it was ensured that the obtained crystal was free from any second phase and the lattice constant was 7.943 Å.

The magnetic measurements were made on a superconducting quantum interference device (SQUID) magnetometer. Figure 1 shows the thermomagnetic curves in the ordered state of the three compounds. For a single crystal of SmAl$_2$, the thermal variation of the magnetization, measured in fields applied along the easy direction of $\langle 111 \rangle$ (see the inset), is presented. This direction of easy magnetization is in agreement with previous results.[9–11] Prior to the measurements, the sample was cooled to 2 K in a field of 1 T applied parallel to the measurement direction, and the data were
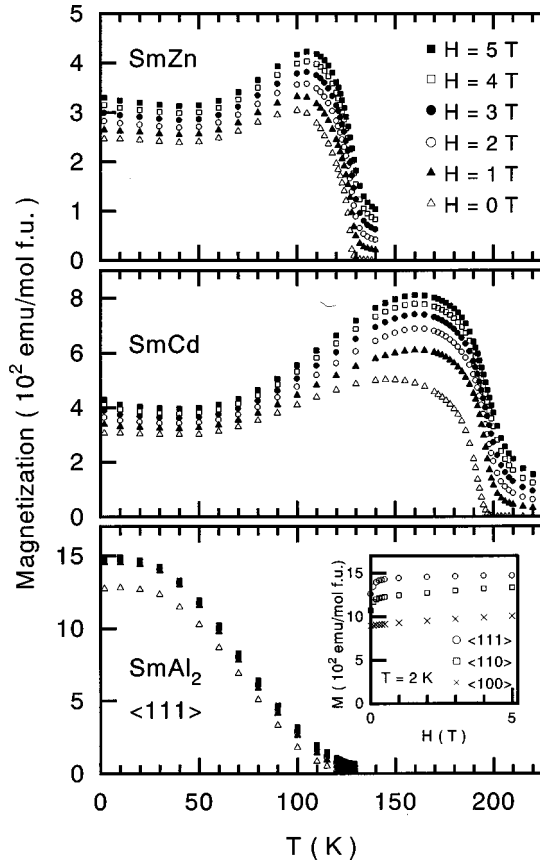
FIG. 1. The thermomagnetic curves for polycrystalline samples of SmZn and SmCd, and that of a single crystal of SmAl$_2$ measured in fields applied along the easy direction of $\langle 111 \rangle$. The inset shows the magnetization of SmAl$_2$ at 2 K as a function of magnetic field applied along the three symmetry directions.
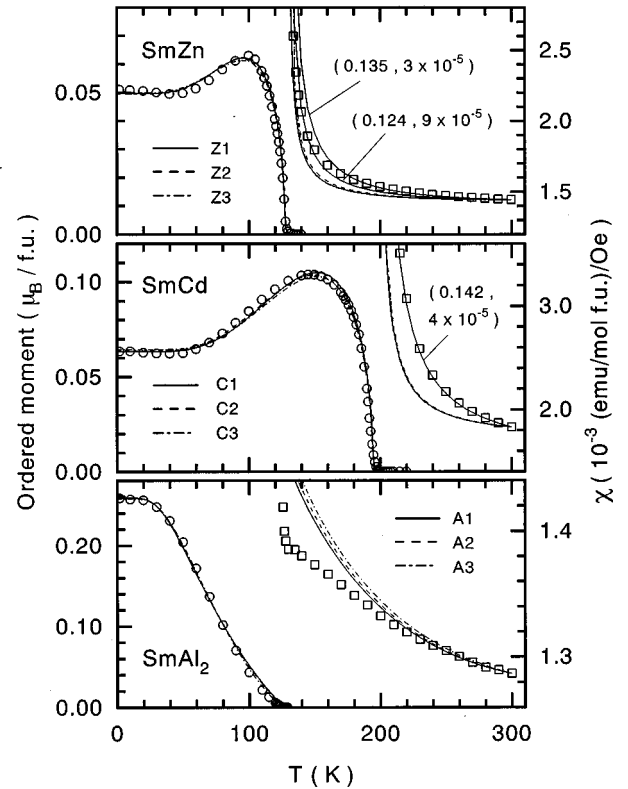

FIG. 2. The examples of the calculated curves for the temperature dependences of the ordered moment and the paramagnetic susceptibility to fit the experiments (open circles and squares). The calculations take into account the lowest two multiplets and the three multiplets, respectively, for the ordered moment and the paramagnetic susceptibility. $Z1$, $Z2$, etc. represent the parameter sets used in the calculations, which are listed in Table I. The spin-orbit interaction constant λ is 430 K.

taken at each temperature with changing the field from 5 T to 0. As for the data in the paramagnetic region, temperature variations of susceptibility are shown in Fig. 2 by the open squares, which are obtained from the magnetization readings linear to the field strength.

In the ordered state, the thermomagnetic curves of SmZn and SmCd have broad maxima and that of SmAl$_2$ has a completely different shape from the other two. The ordering temperatures are 128, 195, and 125 K for SmZn, SmCd, and SmAl$_2$, respectively. The magnitude and the thermal variations of the paramagnetic susceptibilities are also very much dependent on the compounds (note the scale for each compound). The different features of those for SmZn and SmAl$_2$ are worth noting, although they have nearly the same ordering temperatures.

We compared these results with the numerical curves calculated before,[1] and found that it can be easily inferred that the spin moment exceeds the orbital one for SmZn and SmCd, and that the relation in magnitude of the two components is reversed for SmAl$_2$ in the ordered state. Such an interpretation will be quantitatively verified in the next section.

III. ANALYSIS

The experimental values of the ordered moment and the paramagnetic susceptibility have been analyzed with the

model of the Sm^{3+} ion in a metallic matrix. The numerical procedures are almost the same as reported before,[1] with the starting Hamiltonian of the $4f$ electrons:[12–15]

$$\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S} + \mathcal{H}_{\text{cryst}} + \mu_B \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S})$$
$$+ 2\mu_B J\rho \mathbf{H} \cdot \mathbf{S} - 2\mathcal{J}_{ff}\langle \mathbf{S} \rangle \cdot \mathbf{S}, \qquad (1)$$

were $\mathbf{L}$ and $\mathbf{S}$ are, respectively, the orbital and the spin angular momentum operators, $\mathcal{H}_{\text{cryst}}$ is the crystal-field Hamiltonian, μ_B is the Bohr magneton, and $\mathbf{H}$ is the external field. The parameters in the calculations are the interionic exchange $\mathcal{J}_{ff}$, the fourth- and the sixth-order crystal-field parameters $A_4\langle r^4 \rangle$ and $A_6\langle r^6 \rangle$, and the conduction-electron polarization parameter $J\rho$, where J and ρ mean, respectively, the zero-wave-vector component of the exchange integral between the $4f$ and the conduction electrons and the density of states at the Fermi level. The spin-orbit interaction coefficient λ was fixed throughout to be 430 K.

At first, we have fitted the experimental temperature dependence of the ordered moment per formula unit with the calculated curve for each compound. The experimental values for SmZn and SmCd are derived from the magnetization data at 0 T with the assumption that the sample is a nonoriented polycrystal with the easy axis of $\langle 111 \rangle$.[3] The value obtained this way for SmZn at 2 K is $0.051\mu_B$/f.u., giving a good agreement with the spontaneous magnetization of the

TABLE I. The examples of the parameter sets derived from the analysis of the temperature dependence of the ordered moment. The value of either the fourth- or the sixth-order crystal-field parameter indicated by an asterisk was fixed through the analysis, and the rest of the parameters were determined by the least-squares method. ΔE means the calculated energy interval between Γ_7 and Γ_8 of the ground multiplet in the paramagnetic state (the positive value means the case that the former is lower).

	$\mathcal{J}_{ff}$ (K)	$J\rho$	$A_4^0\langle r^4\rangle$ (K)	$A_6^0\langle r^6\rangle$ (K)	ΔE (K)	
SmZn	37.6	0.112	189	0*	169	Z1
	37.6	0.113	160*	−25	155	Z2
	36.8	0.106	220*	12	186	Z3
SmCd	52.7	0.105	215	0*	191	C1
	52.7	0.100	180*	−49	182	C2
	52.7	0.100	250*	14	208	C3
SmAl$_2$	36.2	0.062	50*	111	−11	A1
	36.4	0.059	100*	119	5	A2
	36.9	0.051	200*	139	28	A3

single crystal of 0.055 μ_B/f.u. reported by Givord *et al.*[3] Due to the lack of single-crystal data on SmCd, the easy axis is not established, but the $\langle 111\rangle$ direction is likely, considering it has a chemical and structural similarity to SmZn. The data of SmAl$_2$ are obtained from the values of the magnetization at fields of 5, 4, 3, 2, 1 T by extrapolating them linearly to 0 T, since the demagnetization was observed in a weak-field region less than 1 T (see Fig. 1). In calculating the ordered moment for all the three compounds, therefore, the exchange field was chosen to be parallel to $\langle 111\rangle$.

Figure 2 shows the examples of the fitting results calculated with the reasonable values of the parameter sets, which are tabulated in Table I. The characteristic curves observed experimentally are reproduced extremely well by the calcu-

lations, despite some of the ambiguity in determining the set of the crystal-field parameters. The calculated values of the components in the total moment at 0 K are listed in Table II, together with some results of neutron-diffraction studies.[3,11,16]

The calculated susceptibilities using these parameter sets, on the other hand, do not correspond with the experiments quantitatively, though the discrepancy is small for SmAl$_2$. Here, the temperature-independent values of the sum of the Pauli and the diamagnetic susceptibilities $\chi_{\text{Pauli}}+\chi_{\text{dia}}$ are determined to fit the calculated values with the experimental ones at 300 K, which are about 1.5, 3.8, and 1.0×10^{-4} (emu/mol f.u.)/Oe, respectively, for SmZn, SmCd, and SmAl$_2$.

As is shown in the figure, for SmZn and SmCd, better fits can be obtained with somewhat larger values of $J\rho$ and smaller values of $\chi_{\text{Pauli}}+\chi_{\text{dia}}$ denoted in parentheses for example, where the sets Z1 and C1 are used for the other parameters. Considering that the values of $\chi_{\text{Pauli}}+\chi_{\text{dia}}$ in these cases agree rather well with the susceptibilities of the isostructural nonmagnetic compounds YCd of 9×10^{-5} (emu/mol f.u.)/Oe and LaCd of $6\times10^{-5},$[5,6] 9×10^{-5} (emu/mol f.u.)/Oe,[17] the conduction-electron polarization effect in the paramagnetic state may be different from that in the ordered one due to the change of electronic structure concomitant with the magnetic transition.

The susceptibilities of SmZn and SmCd can be also fitted by the calculations neglecting the crystal fields. In that case, however, $\chi_{\text{Pauli}}+\chi_{\text{dia}}$ takes a negative value and the temperature dependence of the ordered moment cannot be explained. This implies that the analysis without the crystal-field effect is not sufficient quantitative in these cases.

IV. DISCUSSION

The analysis on the ordered moment indicates that, for SmZn and SmCd, the spin moment enhanced by the conduction-electron polarization exceeds the orbital one, and

TABLE II. The values of the total ordered moment and the components at 0 K obtained by the analysis. The minus sign means that the component contributes negatively to the total moment. $Z1$, $Z2$, etc. in the last column mean the parameter sets used in the calculations, which are listed in Table I.

	m_{total} (μ_B)	m_{4f} (μ_B)	$-L_z$	$-2S_z$	m_{cond} (μ_B)	
SmZn	0.05	−0.36	−4.01	3.65	0.41	Z1
	0.05	−0.36	−4.00	3.64	0.41	Z2
	0.05	−0.33	−3.94	3.61	0.38	Z3
	0.06	−0.22 or −0.16			0.28 or 0.22	Ref. 3
SmCd	0.06	−0.34	−4.19	3.85	0.40	C1
	0.06	−0.31	−4.08	3.77	0.38	C2
	0.06	−0.32	−4.15	3.83	0.38	C3
SmAl$_2$	0.26	0.50	4.37	−3.87	−0.24	A1
	0.26	0.49	4.36	−3.87	−0.23	A2
	0.26	0.45	4.27	−3.81	−0.19	A3
	0.23	0.44			−0.21	Ref. 16
	0.23	0.53	3.73	−3.22	−0.30	Ref. 11

that, for $SmAl_2$, the latter is larger than the former. These results are consistent with the neutron-diffraction experiments for SmZn and $SmAl_2$ (see Table II), implying the validity of our analysis on these compounds. The result for SmCd, on which the neutron-diffraction study has not been done, seems also a plausible one, considering an analogy between SmZn and SmCd.[18] Note that, in the present analysis, the value of each parameter can be determined with little ambiguity, except the crystal-field parameter sets. To obtain the unique solutions for the crystal fields, additional data will be needed.

It is of interest to note that all the values of $J\rho$ derived from the ordered moment are smaller than those of pure Sm metal estimated before.[1,19–21] This reminds us of the negative polarization on the site of the nonmagnetic counterpart in the intermetallics due to the orbital mixing. Indeed, for cubic Laves phase compounds RAl_2 (R=rare earth), such a polarization on the Al site has been suggested experimentally.[22]

One enigma of the derived parameter is the sixth-order crystal field for $SmAl_2$. The origin of this large value is unclear at present, which makes the value of the effective charges, converted using a point-charge model, quite large. Since the sixth-order field has no influence within the ground multiplet of $J=5/2$, the energy split between Γ_7 and Γ_8 is rather small (see Table I). The largeness of the sixth-order field, however, causes a wide split of the first excited multiplet of $J=7/2$. Then, further examination on this point will be performable using the neutron spectroscopy technique, for instance.

The sign reversal of the Knight shift of Al nuclei in $SmAl_2$ seems worth mentioning here. Such a change in sign of the Knight shift at the nonmagnetic site, characteristic of some kinds of Sm compounds, has been suggested for $SmAl_2$ at around 150 K, and ascribed to the unique sign behavior of the paramagnetic linear response $\langle \mathbf{S} \rangle / \mathbf{H}$ due to the second-order Zeeman effect.[23] As for $SmAl_2$ itself, however, the failure to observe it was subsequently reported.[24] Our calculations for this compound, on the other hand, show that the difference in magnitude between the spin and the orbital contributions to the total moment gradually vanishes as the temperature approaches the ordering point. When the compensation between the two occurs in the vicinity of the ordering point, the crossover temperature, at which $\langle \mathbf{S} \rangle / \mathbf{H}$ crosses the zero line, is expected to be very close to the ordering point, if it ever exists.[1] Such a delicate situation is thought to be the cause of the above controversy. With the parameter sets $A1–A3$ of Table I, the sign reversal does not appear in the calculated curves of $\langle \mathbf{S} \rangle / \mathbf{H}$, but a little change of the parameters actually causes the appearance of it just above the ordering point. The observation of the Knight-shift crossover for $SmAl_2$ in the paramagnetic region must be, then, a close call. It might be sensitive to the quality of the sample.

V. CONCLUSION

We have studied the temperature dependences of the ordered moment and the paramagnetic susceptibility of ferromagnetic intermetallics SmZn, SmCd, and $SmAl_2$, and analyzed the experimental results by the calculations for the Sm^{3+} ion in metals, taking into account the excited multiplets of the $4f$ electrons, the interionic exchange, the crystal fields, and the conduction-electron polarization. The exotic thermomagnetic behavior was described very well within the framework, and the separation of the $4f$-spin, $4f$-orbital, and conduction-electron component of the total ordered moment was done with little ambiguity. Some pieces of information on the local environment of Sm^{3+} in these compounds were also derived through the analysis, such as the difference between the conduction-electron polarization effect in the ordered state and that in the paramagnetic one, the strong sixth-order crystal field acting on Sm^{3+} in $SmAl_2$, though the reasons are uncertain now. It should be noted again that it is the unique properties of Sm^{3+} that make these analyses possible, namely the marginal cancellation and the different temperature dependence of the spin moment and the orbital one, and, besides in metallic cases, the sizable contribution of the conduction-electron polarization to the total moment.

Finally, we wind up the paper by recording a classification of some types of the temperature dependence of the ordered Sm^{3+} moment. According to the calculations, the spin part changes less in magnitude at low temperatures and varies more steeply around the ordering point compared with the orbital part. Therefore, it can be said, by analogy with the various M-T curves of ferrimagnets, that the thermal variation of the total ordered moment having a broad maximum means that the spin part, including the conduction-electron polarization, is larger than the orbital one, and that resembling the M-T curve of $SmAl_2$ means the opposite case. The possible thermal variation having the compensation temperature T_{comp} must correspond to the case where the spin moment exceeds the orbital one above T_{comp} and the situation reverses below T_{comp}. These criteria will be helpful to the interpretation of the magnetism of materials containing Sm^{3+}.

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