

Valence states of Sm in SmRuSn₃

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To obtain a better insight into the nature of valence states of Sm ions in SmRuSn₃ and to verify the differing conclusions reached by T. Fukuhara, I. Sakamoto, and H. Sato [J. Phys. Condens. Matter **3**, 8917 (1991)] and C. Godart *et al.* [Phys. Rev. B **48**, 16 402 (1993)], we have systematically analyzed the magnetic-susceptibility data by considering the effects of crystalline electric field, exchange interaction, and valence fluctuation. In this compound, Sm ions occupy two different sites, *6d* and *2a*, in the ratio of 3:1. Our analysis shows that Sm ions at the *6d* site are in a trivalent state and those at the *2a* sites are in a valence fluctuating state. This supports the claim made by C. Godart *et al.* [Phys. Rev. B **48**, 16 402 (1993)].

I. INTRODUCTION

Fukuhara, Sakamoto, and Sato¹ reported transport and magnetic properties of RRuSn₃ (*R*=La, Ce, Pr, Nd, and Sm), in which SmRuSn₃ orders antiferromagnetically and was claimed to be a new valence fluctuating compound on the basis of lattice constant anomaly and the magnitude of paramagnetic susceptibility. These authors¹ obtained a qualitative fit to the magnetic susceptibility in the temperature range of 150–300 K, without considering the effect of crystalline electric field and exchange interaction and by assuming that 80% of Sm ions are in trivalent state and the remaining 20% Sm ions are in divalent state. Further, they did not consider the fact, that this structure has two inequivalent Sm sites.

Recently, Godart *et al.*² reinvestigated the magnetic, thermal and transport properties of SmRuSn₃. This compound orders antiferromagnetically at about 6 K.^{1,2} On the basis of magnitude of entropy calculated from the heat-capacity measurements and by considering the fact that Sm ions are distributed among two inequivalent crystallographic sites, *6d* and *2a* with the population ratio of 3:1, it was concluded² that Sm ions at the *6d* site are in a trivalent state and, therefore carry a magnetic moment in the ground state, on the other hand, Sm ions at the *2a* sites are either divalent or valence fluctuating and, therefore have a nonmagnetic ground state. Interestingly, in their powder x-ray diffraction measurements, these authors² did not observe any anomaly in the lattice constant of SmRuSn₃ in relation to those of other isostructural analogues RRuSn₃ (*R*=La, Ce, Pr, and Nd). This is contrary to the results obtained by Fukuhara, Sakamoto, and Sato.¹

To obtain a better insight into the nature of valence states of Sm ions in SmRuSn₃ and to verify the differing conclusions reached by Fukuhara, Sakamoto, and Sato¹ and Godart

et al.,² we have systematically analyzed their experimental observations. Strong influence of exchange interaction is clearly observed from the low-temperature magnetic susceptibility and heat capacity studies. The entropy calculated from the heat capacity measurements shows that there is a considerable effect of crystalline electric field. High-temperature paramagnetic susceptibility indicates the effect of valence fluctuation. In this theoretical analysis of experimental results obtained by Godart *et al.*,² we have taken all these three effects into consideration and have been able to obtain a good fit to the experimentally observed magnetic susceptibility data in the entire range of temperature, 6–300 K.

II. ANALYSIS

We have analyzed the experimental results by taking into account all the complexities involved in the calculations with a minimum possible number of parameters. In SmRuSn₃, Sm ions have two inequivalent sites *6d* ($\frac{1}{4}, \frac{1}{2}, 0$) and *2a* (0,0,0) in the ratio of 3:1 with the site symmetry tetragonal and cubic, respectively. The magnitude of entropy calculated from the heat capacity measurements by Godart *et al.*² shows that the ground state $J = \frac{5}{2}$ of Sm³⁺ ion is split by crystalline electric field to give a doublet as a crystal field ground state. We assume that the overall features of crystalline electric field potential, at both the sites, can be reasonably described by cubic symmetry. This assumption considerably limits the number of crystal field parameters.

The Hamiltonian of the system consisting of the spin-orbit coupling, crystalline electric field, Zeeman and exchange field terms,

$$\mathcal{H} = \lambda \vec{L} \cdot \vec{S} + \mathcal{H}_c + \beta \vec{H} \cdot (\vec{L} + 2\vec{S}) + \mathcal{H}_{ex}, \quad (1)$$

is diagonalized within the substates arising from the lowest two multiplets of Sm^{3+} ($J=\frac{5}{2}$ and $\frac{7}{2}$) and four lowest multiplets of Sm^{2+} ($J=0, 1, 2,$ and 3) to obtain the energy and eigenfunctions of respective Sm ions. We neglected higher J multiplets to reduce the size of the matrix to be diagonalized and because they lie far off in energy so that their contribution to the susceptibility, either directly or indirectly, is negligible.

The crystal field Hamiltonian in terms of tensor operators, $C_m^{(n)}$, for cubic symmetry can be written as³

$$\begin{aligned} \mathcal{H}_c = & 8A_4\langle r^4 \rangle \sum [C_0^{(4)} + (5/14)^{\frac{1}{2}}(C_{-4}^{(4)} + C_{+4}^{(4)})] \\ & + 16A_6\langle r^6 \rangle \sum [C_0^{(6)} - (7/2)^{\frac{1}{2}}(C_{-4}^{(6)} + C_{+4}^{(6)})], \end{aligned} \quad (2)$$

where $A_4\langle r^4 \rangle$ and $A_6\langle r^6 \rangle$ determine the strength of crystal field. The matrix elements of the $C_m^{(n)}$ between different states were calculated using the method given by Wybourne.⁴ For cubic crystal field, we have maintained only fourth-order terms and neglected the sixth-order terms. We have also neglected the cubic crystal field splitting for excited state, $J=2$ and 3 for Sm^{2+} ions. Therefore, crystalline electric field interaction is determined, for both sites, by using only one independent parameter.

The exchange interaction, in molecular field framework, above Néel temperature is given by

$$\mathcal{H}_{\text{ex}} = -2zJ\langle \vec{S} \rangle \cdot \vec{S}. \quad (3)$$

Here z is the number of nearest equivalent neighbors interacting with the exchange interaction J , and $\langle S \rangle$ is the expectation value of the spin operator S . In our calculation an iterative procedure is used to calculate $\langle S \rangle$ self-consistently. The details of this procedure are discussed by Marathe and Mitra.⁵

Throughout our calculation, we have fixed the exchange parameter zJ in Eq. (3) based on the expression

$$zJ = -\frac{3kT_N}{2S(S+1)} \quad (4)$$

derived on the basis of the two sublattice model of molecular field theory.⁶ By considering Néel temperature (T_N) equal to 6.7 K (from experimental magnetic susceptibility) and effective spin S equal to $\frac{1}{2}$ for doublet crystal field ground state, we obtained $zJ = -9.4 \text{ cm}^{-1}$. The energy separation between the ground ($J=\frac{5}{2}$) level and the first excited ($J=\frac{7}{2}$) level for Sm^{3+} is fixed to be 1000 cm^{-1} based on the spectroscopic data⁷ for Sm^{3+} .

We have analyzed all the three possible situations arising from the conclusions of Fukuhara, Sakamoto, and Sato¹ and Godart *et al.*,² (a) all the Sm ions in SmRuSn_3 are valence fluctuating and order magnetically; (b) the Sm ions at the $6d$ site are trivalent which order magnetically and the Sm ions at the $2a$ sites are purely divalent; and (c) the Sm ions at the $6d$ site are trivalent which order magnetically and the Sm ions at the $2a$ sites are valence fluctuating.

When we consider all the Sm ions to be in a valence fluctuation state, our results show considerable deviation from the experimental results. This rules out the claim made by Fukuhara, Sakamoto, and Sato¹ that SmRuSn_3 with *all*

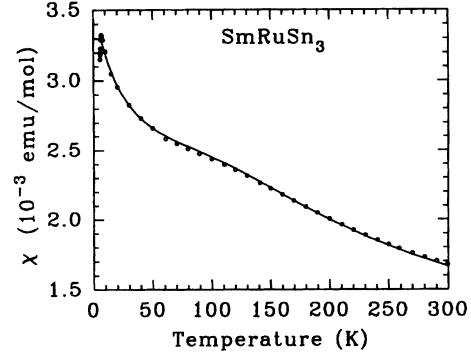


FIG. 1. Observed and calculated magnetic susceptibility of SmRuSn_3 . The circles denote the experimental data (Ref. 2) and the solid line is the result of the calculation based on the crystal field, exchange, and valence fluctuation parameters (see text).

the Sm ions in valence fluctuating state. When we considered all Sm ions at the $6d$ site to be trivalent and the Sm ions at the $2a$ sites to be purely in a divalent state, the calculated magnetic susceptibility did not agree with the observed results. We obtained, as also observed by Fukuhara, Sakamoto, and Sato,¹ a qualitative fit to the magnetic susceptibility data in the high-temperature region, when we consider approximately the contribution to the total susceptibility from Sm^{3+} and Sm^{2+} ions to be in the ratio of approximately 81:19 instead of 75:25. The additional 6% contribution to the total susceptibility from Sm^{3+} can be reconciled, only if we consider the Sm ions at the $2a$ site are valence fluctuating.

Our results agree exactly with the experimentally observed magnetic susceptibility, for the temperature range 6 to 300 K, when we assume that 75% Sm ions at the $6d$ site are trivalent which order antiferromagnetically and the remaining 25% of Sm ions at the $2a$ site are valence fluctuating. The calculated and experimental susceptibility are shown in Fig. 1. The calculated crystalline electric field level scheme for Sm^{3+} ion at the $6d$ site is shown in Fig. 2 and energy level scheme for $\text{Sm}^{2+} - \text{Sm}^{3+}$ ions at the valence fluctuating $2a$ site is shown in Fig. 3. We obtained the best fit to the experimental result with the following parameters; (a) the cubic crystal field parameter $A_4\langle r^4 \rangle = 480 \text{ cm}^{-1}$; (b) the en-

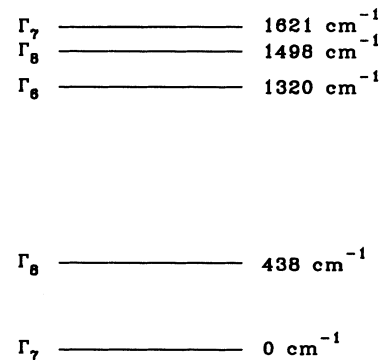


FIG. 2. Crystal field level scheme for the ground state $J=\frac{5}{2}$ and the first excited state $J=\frac{7}{2}$ of Sm^{3+} ion in SmRuSn_3 at the $6d$ site, calculated by using the cubic crystal field parameter $A_4\langle r^4 \rangle = 480 \text{ cm}^{-1}$.

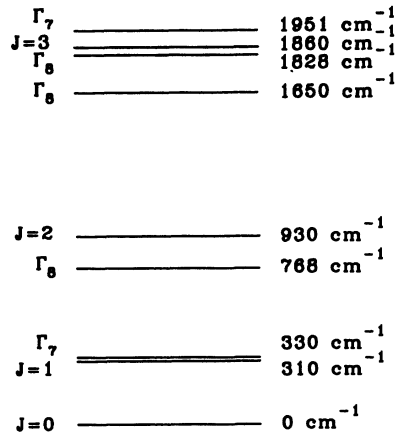


FIG. 3. Energy level scheme of Sm²⁺–Sm³⁺ ions in SmRuSn₃ at valence fluctuating 2a site.

ergy separation between $J=0$ for Sm²⁺ and Γ_7 states for Sm³⁺ in valence fluctuation state = 330 cm⁻¹; and (c) the energy separation (λ) between $J=0$ and $J=1$ states of Sm²⁺ = 310 cm⁻¹.

The spin-orbit coupling constant λ for Sm²⁺ ion seems to be slightly higher than the empirical value of 290 cm⁻¹ re-

ported in the literature for Sm²⁺ ions.⁷ We found it necessary to use an increased value of this parameter to 310 cm⁻¹ in order to obtain a satisfactory fit to the susceptibility data, particularly in the range of 50–100 K. This kind of increase in the spin-orbit coupling parameter λ is also found experimentally for the compounds CeIn_(1-x)Sn_x.⁸ Within the approximations involved in the calculation, the set of parameters is unique.

This clearly establishes that the valence state properties of Sm ions in SmRuSn₃ are site dependent. Similar kind of behavior is also seen in other rare earth containing compounds. For example, in Ce₂Sn₅,⁹ Ce has two inequivalent sites in the ratio of 1:1. At one site Ce ions are in a trivalent state and order antiferromagnetically and at the other site the Ce ions are in valence fluctuation state.

To conclude, our rigorous and systematic analysis clearly shows that, *not all* the Sm ions in SmRuSn₃ are valence fluctuating as claimed by Fukuhara, Sakamoto, and Sato.¹ Instead, Sm ions at the 6d sites are trivalent and are responsible to antiferromagnetic ordering at 6 K and those remaining Sm ions at the 2a sites are valence fluctuating. This supports the claim made by Godart *et al.*² From our analysis, we obtain the crystal field splitting between Γ_7 and Γ_8 states of Sm³⁺ ions to be 438 cm⁻¹. It would be interesting to measure the crystal field splitting experimentally, say, for example, by Raman spectroscopy etc.

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