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# Valence state of Sm in $SmRuSn_3$

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T. Fukuhara, I. Sakamoto, and H. Sato [J. Phys.: Condens. Matter **3**, 8917 (1991)] reported valence fluctuations of Sm ions in $SmRuSn_3$, which orders antiferromagnetically at 6 K. We have carried out x-ray, microprobe, heat-capacity, susceptibility, and resistivity measurements on a sample of nearly the same stoichiometry. There are two inequivalent Sm sites in $SmRuSn_3$ and from the analysis of our data we conclude that Sm ions at one site are in the trivalent state and those at the second site are either divalent or weakly valence fluctuating.

## I. INTRODUCTION

Transport and magnetic properties of $R$RuSn$_3$ compounds ($R=$La, Ce, Pr, Nd, and Sm) have been reported by Fukuhara *et al.*[1,2] $CeRuSn_3$ is a heavy-fermion compound with a large value of the coefficient of the electronic specific heat, $\gamma=1.67$ J/mol K$^2$ at 0.6 K. The compounds containing Pr and Nd do not order magnetically at least down to 1.8 K. $LaRuSn_3$ becomes superconducting at 1.5 K.[1,3] Interestingly, $SmRuSn_3$ was claimed to be a new valence-fluctuating compound which orders antiferromagnetically at 6 K.[1] The last observation is noteworthy as only a few compounds are known in which Sm ions undergo valence fluctuations. The two known examples, SmS under pressure[4] and $SmB_6$ under ambient conditions,[5] are binary systems in contrast to $SmRuSn_3$, which is a ternary. In addition, the occurrence of a magnetic transition at 6 K in $SmRuSn_3$ would be quite unusual keeping in view the general observation that valence-fluctuating compounds of Ce, Sm, Eu, and Yb do not order magnetically.[6] Both SmS under pressure and $SmB_6$, for example, are Pauli paramagnets at low temperatures. Fukuhara, Sakamoto, and Sato[1] reached their conclusion concerning the existence of valence fluctuations in $SmRuSn_3$ mainly from the observation of a lattice-constant anomaly and the magnitude of the paramagnetic susceptibility. The authors found that the lattice constant showed an appreciable deviation from the value expected on the basis of lanthanide contraction for trivalent rare-earth ions, which is one of the characteristic features of the valence-fluctuating compounds. The paramagnetic susceptibility of $SmRuSn_3$ was found to be larger, in the range 50–300 K, than the theoretically calculated susceptibility of a $Sm^{3+}$ ion. A good fit to the experimental susceptibility data, in the range from 300 to about 150 K only, was obtained by these authors by assuming that 20% of Sm ions were in the divalent state and using the theoretical values of the magnetic susceptibility of divalent and trivalent free Sm ions, respectively. The thermoelectric power of $SmRuSn_3$ shows a large positive maximum of 20 $\mu$V K$^{-1}$ near 150 K, and Fukuhara, Sakamoto, and Sato[1] mention that a similar behavior is seen in $CeSn_3$, which is a valence-fluctuating compound.

Though the data obtained by Fukuhara, Sakamoto, and Sato[1] on $SmRuSn_3$ can in principle lend itself to an interpretation in terms of a valence-fluctuating state of Sm ions, we felt the evidence for such a conclusion was not sufficient and needed further investigation for the following reasons. Fukuhara, Sakamoto, and Sato,[1] for example, find that isostructural $CeRuSn_x$ has an extended solid-solution range for $2.85<x<3.15$ and for compositions $x<3$ the lattice parameter shows a marked increase. They also find that the lattice constant of $NdRuSn_{2.91}$ is slightly larger than $NdRuSn_3$. A similar composition dependence (on Sn) of the lattice parameter in the case of the Sm compound cannot be ruled out. The temperature dependences of the susceptibility, resistivity, magnetoresistivity, and thermoelectric power of $CeRuSn_x$ alloys show considerable differences as a function of Sn composition. The thermopower of $CeRuSn_{3.15}$ and $CeRuSn_{2.85}$ is, for example, an order of magnitude larger than that for $CeRuSn_3$. Fukuhara, Sakamoto, and Sato[1] do not correlate these differences with any change in the valence state of the Ce ions. They find that the paramagnetic susceptibilities of $CeRuSn_x$ alloys for $x = 2.85$, 2.91, and 3.0 (Fig. 11 of Ref. 1) are similar in magnitude in the range 300–50 K. Second, it is very important to note that there are two inequivalent Sm sites in $SmRuSn_3$. As a result, Sm ions occupying these two inequivalent lattice sites could exhibit different valence states, forming a heterogeneous static mixed valence system, a point not dwelt upon by Fukuhara, Sakamoto, and Sato[1] when proposing valence fluctuations in $SmRuSn_3$. Such a behavior has, for example, been reported in $Ce_2Sn_5$,[7,8] in which there are two inequivalent lattice sites for Ce. On the other hand, the valence-fluctuating state arising due to the interconfiguration fluctuation of the rare-earth ion between the two integral valence states would give rise to temperature-dependent anomalies in many of the physical properties, though it would also exhibit an anomaly in the lattice constant. In order to clarify these aspects, we have prepared a well-characterized sample of $SmRuSn_3$ and investigated its physical properties. We describe here the results of these investigations.

## II. EXPERIMENTAL DETAILS

The sample of $SmRuSn_3$ weighing about 6 gm was prepared by arc melting the constituents in an inert atmosphere of argon. The single-phase character of our sample was confirmed using x-ray diffraction. Electron microprobe analysis was carried out to determine the composition and the presence of small amounts of parasitic phases which would escape detection by x-ray diffraction. The magnetic susceptibility was measured, using a Faraday magnetometer, in an external field of 4 kOe over the temperature interval $4.2\ \mathrm{K} < T < 300$ K. The electrical resistivity was measured using a four-probe dc technique, in an automated setup, from 1.5 to 300 K. The heat capacity of $SmRuSn_3$ and the reference nonmagnetic material $LaRuSn_3$ was measured using a semiadiabatic heat-pulse method, on a home-built automated setup from 2 to 25 K.

## III. RESULTS AND DISCUSSION

$RRuSn_3$ ($R =$ La, Ce, Pr, Nd, and Sm) compounds belong to the cubic $Pm3n$ space group.[9] It is important to note that there are two crystallographically inequivalent lattice sites for $R$ in this structure, i.e., $2a$ (0,0,0) and $6d$ $(\frac{1}{4},\frac{1}{2},0)$, respectively. The site symmetry of $2a$ and $6d$ sites is cubic and tetragonal, respectively. We could index all the lines of the x-ray-diffraction pattern of our sample on the basis of lattice parameter $a = 9.666$ Å. Our value is considerably different from that reported by Fukuhara, Sakamoto, and Sato[1] (Fig. 1). It is clear that the lattice-constant anomaly observed by Fukuhara, Sakamoto, and Sato[1] does not exist in our sample and that we observe the normal lanthanide contraction behavior of trivalent rare-earth ions. Normally, this could imply that all the Sm ions are in the trivalent state. However, such a conclusion is not corroborated by our heat-capacity and magnetic-susceptibility data. In order to check the composition and the homogeneity of our sample, we carried out a microprobe analysis. It showed that the sample is homogeneous (Fig. 2) and only contains some small inclusions ($\approx 50\ \mu m^2$), some of them being pure Sn and some having a composition "SmSn." The mean composition that we determine through the sample (normalized to Ru) is $Sm_{0.98}RuSn_{3.10}$, in fairly good agreement with the expected 1:1:3 composition.

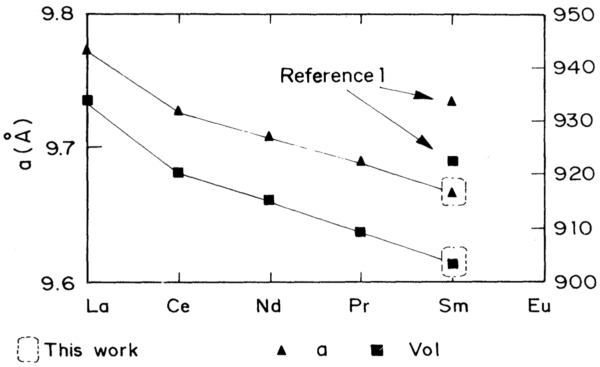

FIG. 1. Lattice parameter and volume of the unit cell of $RRuSn_3$ ($R =$ La, Ce, Pr, and Nd) according to Ref. 9 and of $SmRuSn_3$ according to Ref. 1 and this work.

Figure 3 depicts the heat capacity $C$ of $SmRuSn_3$ and of the reference nonmagnetic analog $LaRuSn_3$ in the range 2–25 K. An anomaly with a peak height exceeding 9 J/mol K clearly demonstrates the transition to the magnetically ordered state in the Sm compound. We deduce a value of 6 K for the transition temperature, taken as the temperature at which the magnetic heat capacity exhibits its maximum. Our value is in good agreement with that reported by Fukuhara, Sakamoto, and Sato[1] who obtained it from the resistivity and susceptibility data. We do not observe any anomaly in the heat-capacity data of $LaRuSn_3$ in the range investigated. The $C/T$ vs $T^2$ plot of $LaRuSn_3$ is linear in the range 2–5 K. A least-squares fit to the data gives $\gamma = 3$ mJ/mol K$^2$ and $\beta = 1.806$ mJ/mol K$^4$, where $\beta$ represents the lattice contribution to the heat capacity. The $\gamma$ value of $LaRuSn_3$ is typical of a normal intermetallic compound. A value of 175 K is obtained for the Debye temperature $\Theta_D$ by using the relation $\Theta_D^3 = 1\,943\,700/\beta$, where $\beta$ is in the units of mJ/g atom K$^4$.

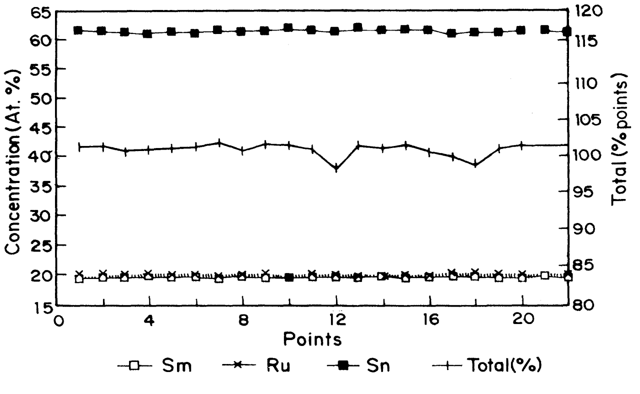

FIG. 2. Microprobe analysis results on $SmRuSn_3$.

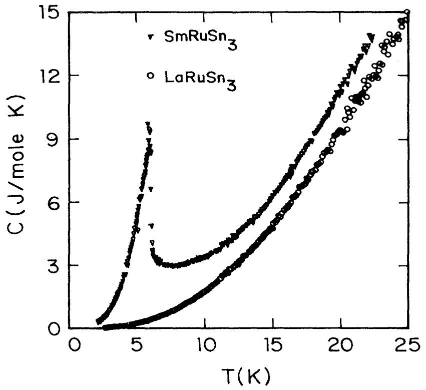

FIG. 3. Heat capacity of $SmRuSn_3$ and $LaRuSn_3$ between 2 and 25 K.

One can deduce some information on the valence state of Sm in $SmRuSn_3$ from the entropy associated with the magnetic transition, and it is of relevance in the context of the report of Fukuhara, Sakamoto, and Sato[1] on the valence fluctuations of the Sm ions in this material. To estimate this entropy, one must subtract the normal-lattice, conduction-electron, and other possible contributions to the total specific heat. For this purpose, we assume that the lattice and electron contributions in the Sm compound are the same as in nonmagnetic $LaRuSn_3$. After subtraction, we find a nearly temperature-independent $C/T$ value of 80 $mJ/mol\,K^2$ in the range 14–22 K in $SmRuSn_3$. An extrapolation of the heat-capacity data below 2 K to $T=0$ (taking $C/T=80$ $mJ/mol\,K^2$ at $T=0$) has been made, and the entropy was estimated up to 16 K. The entropy thus obtained is 3.4 J/mol K.

A $C/T$ value of 80 $mJ/mol\,K^2$ in the region of 14–22 K is a rather large value and could include Schottky contributions from crystal-field split levels as discussed later. If the Schottky contribution is dominant, then one can calculate an upper limit to the entropy associated with the magnetic order by taking $C/T$ at $T=0$ to be 3 $mJ/mol\,K^2$, which is the value obtained for $LaRuSn_3$ (for which there are no crystal-field effects). In this case, we obtain a magnetic entropy of 4.2 J/mol K. In relating the magnitude of entropy to the valence state of the Sm ions at the two inequivalent sites, we have to keep in mind that in the cubic-crystal-field environment, the $J=\frac{5}{2}$ level of the trivalent Sm ion would split into a doublet and a quartet. A doublet ground state would give an entropy of $R\ln 2$ (=5.76 J/mol K). On the other hand, a quartet can be approximated by an effective spin of $\frac{3}{2}$ and it would give rise to an entropy of about $R\ln 4$ (=11.5 J/mol K) if the quartet is the ground state. As already mentioned, the local symmetry of the $2a$ sites is cubic and that of the $6d$ sites is tetragonal. For the latter, the $(2J+1)$-fold degenerate level of trivalent Sm ions would be split into three doublets by the crystal fields. The two Sm sites $2a$ and $6d$ in $SmRuSn_3$ are in the ratio 1:3. If the Sm ions at both sites are trivalent and order magnetically, an entropy of at least $R\ln 2$ (5.76 J/mol K) is expected, which is much larger than what is observed. The discrepancy is removed if we attribute the observed magnetic entropy only to the $6d$-site Sm ions as the entropy associated with magnetic ordering would get reduced proportionately, giving the value 4.32 J/mol K (i.e., $\frac{3}{4}R\ln 2$), which is close to our estimated value for the case $\gamma=3$ $mJ/mol\,K^2$. This would imply that the $2a$-site Sm ions are divalent as $Sm^{2+}$ has total angular momentum $J=0$ and is nonmagnetic. It is easy to find that the reverse situation; i.e., $2a$-site Sm being trivalent and the $6d$ being nonmagnetic is unlikely as the entropy values differ considerably. Thus, based on entropy considerations, our heat-capacity data strongly suggest a site-dependent magnetic response of the Sm ions in $SmRuSn_3$.

A similar situation occurs in $Ce_2Sn_5$. This material has two inequivalent Ce sites in the ratio 1:1, and it orders magnetically at 2.9 K.[7] The salient features of the heat-capacity measurements of $Ce_2Sn_5$ are the following: The entropy reaches a value of about $0.4R\ln 2$ at 10 K. A high-temperature ($9\ K<T<16\ K$) extrapolation yields $C/T$ of 56 $mJ/mol\,K^2$ at $T=0$ K. The nonmagnetic Ce ions (50%) in $Ce_2Sn_5$ are inferred to be in the valence-fluctuating state.

As mentioned above, a nearly temperature-independent $C/T$ of 80 $mJ/mol\,K^2$ between 14 and 22 K is observed. If we assume this to arise from the interaction of Sm $4f$ electrons with the conduction-band electrons, it would imply that some Sm ions are in a valence-fluctuating state in $SmRuSn_3$ as such materials have an enhanced value of the Sommerfeld coefficient $\gamma$.[6] The large $\gamma$ values in the valence-fluctuating materials are believed to be associated with an appreciable hybridization of the $4f$ state with the conduction-electron-band states which lead to a renormalized large electronic density of states at the Fermi level. But as already mentioned above, the existence of low-lying crystal-field levels in rare-earth compounds can also lead to large heat capacities (Schottky contribution), which may be interpreted, erroneously, as arising from valence fluctuations or heavy-fermion behavior. For example, in $CeGa_2$, the crystal-field levels are three doublets at 0, 62.5, and 310 K.[10] The material orders magnetically at 10 K. The extrapolation of high-temperature heat capacity from above the magnetic ordering temperature gives a $\gamma$ value of 340 $mJ/mol\,K^2$. Subtracting the heat capacity of $LaGa_2$ yields a $\gamma$ value of 190 $mJ/mol\,K^2$, which would suggest that $CeGa_2$ is a modest heavy-fermion material. However, when the crystal-field contribution is included, the final value of $\gamma$ turns out to be only about 30 $mJ/mol\,K^2$. Since the crystal-field-level spectrum has not yet been reported for $SmRuSn_3$, an unambiguous interpretation of the modestly large $C/T$ above the magnetic ordering temperature cannot be made. A relatively small energy separation between the crystal-field split levels is not uncommon in Sm compounds. For instance, in cubic $SmPb_3$ and $SmPd_3$ the energy separation is 60 and 50 K, respectively.[11]

Figure 4 depicts the magnetic susceptibility of $SmRuSn_3$. The theoretical magnetic susceptibility of the free divalent and trivalent Sm ions is also plotted.[12] A cusp in the susceptibility occurs at 6.7 K and indicates that the magnetic ordering is antiferomagnetic in nature.

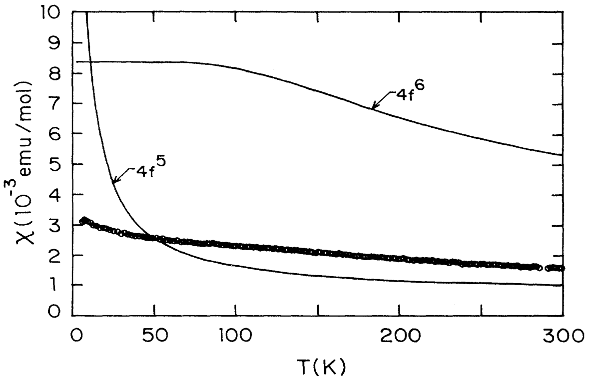

FIG. 4. Magnetic susceptibility of $SmRuSn_3$. For comparison, the susceptibility of free $Sm^{2+}$ and $Sm^{3+}$ ions, taken from Ref. 12, is also plotted.

Normally, the polycrystalline paramagnetic susceptibility of rare-earth compounds shows a Curie-Weiss behavior and the effective paramagnetic moments are close to the free-trivalent-ion value. In Sm compounds, however, there are additional contributions from the excited levels of the *LS* multiplet structure due to a relatively small energy separation and, therefore, the susceptibility often does not exhibit a Curie-Weiss behavior. Crystal fields can also admix the ground and excited levels, thereby affecting the susceptibility. An additional source of complication in the quantitative analysis of the susceptibility in the present case arises due to the nonmagnetic nature of 2*a*-site Sm ions as strongly suggested by the heat-capacity measurements. Therefore, we shall restrict ourselves to a qualitative interpretation of our data. The susceptibility of our sample at 300 K is $1.55\times10^{-3}$ emu/mol and exceeds the free-trivalent-ion value by more than 50%. The susceptibility of $LaRuSn_3$ was also measured at a few selected temperatures between 300 and 20 K, and we obtained a temperature-independent diamagnetic susceptibility of $0.13\times10^{-3}$ emu/mol, giving a corrected susceptibility of $1.68\times10^{-3}$ emu/mol for the Sm compound at 300 K. A check of the susceptibility data reported in the literature on the well-known intermetallic compounds of trivalent samarium shows that the 300-K value of the susceptibility is nearly equal to $1\times10^{-3}$ emu/mol in all of them. The enhanced susceptibility of $SmRuSn_3$ at the higher temperatures (including 300 K) where the effects of crystal fields are marginal can be readily explained if the Sm ions at the 2*a* sites are divalent as inferred from entropy considerations. Taking the $Sm^{2+}$:$Sm^{3+}$ ratio as 1:3 and using the free-ion susceptibility values, a value of $2.1\times10^{-3}$ emu/mol is obtained, which is larger than the experimental value. The magnitude of the susceptibility thus indicates that the population of $Sm^{2+}$ in our sample is less than 25%. It is quite possible that some amount of atomic disorder is present such that some of the 2*a*-site Sm ions are occupying Ru/Sn sites where they may be in a trivalent state. It is not necessary that such off-site randomly placed Sm ions participate in the magnetic transition at 6 K. It may also be possible that the 2*a*-site Sm ions are in a weakly valence-fluctuating state; their contribution to the susceptibility would depend upon the relative fractions of $Sm^{2+}$ and $Sm^{3+}$ at the 2*a* site, and it would be smaller than for the case where the 2*a*-site Sm ions were in the pure divalent state. Our data cannot distinguish between these two possibilities.

It is interesting to note that we do not observe any lattice-constant anomaly in our sample even though about 15% of Sm ions, as estimated from the susceptibility at 300 K, are in the divalent state. It may so happen that the lattice expansion due to divalent Sm ions is canceled by an opposite effect which arises either due to the slight off stoichiometry of our sample or atomic disorder. In the $RRuSn_3$ compounds, tin atoms form strings which are connected by Ru atoms to a framework with cagelike voids occupied by the rare-earth ions. Such a geometrical feature may also reduce the effect of the relatively small population of divalent Sm ions on the average unit-cell volume.

Finally, we show in Fig. 5 the electrical resistivity of $SmRuSn_3$ as a function of temperature. The resistivity decreases with temperature as is expected in a normal metal. We obtain a value of 280 $\mu\Omega$ cm for the resistivity at 295 K, which is in good order-of-magnitude agreement with that reported by Fukuhara, Sakamoto, and Sato.[1] Near the magnetic transition our results are, however, in disagreement with those of Fukuhara, Sakamoto, and Sato.[1] As seen in Fig. 5, the resistivity is lowered at the magnetic transition, which is due to the freezing of the spin-disorder scattering of the conduction electrons. In contrast Fukuhara, Sakamoto, and Sato[1] observed an increase in the resistivity at the magnetic transition in their sample. They interpreted the increase in the resistivity below the magnetic ordering temperature as due to the formation of an antiferromagnetic gap. The magnetic superzone boundaries in antiferromagnets arise because the periodicity of the magnetic structure is different from that of the crystal structure. Since the lattice constant of our sample is different from the one studied by Fukuhara, Sakamoto, and Sato,[1] we can only speculate that the different resistivity response below the ordering temperature in the two samples is somehow related to that feature.

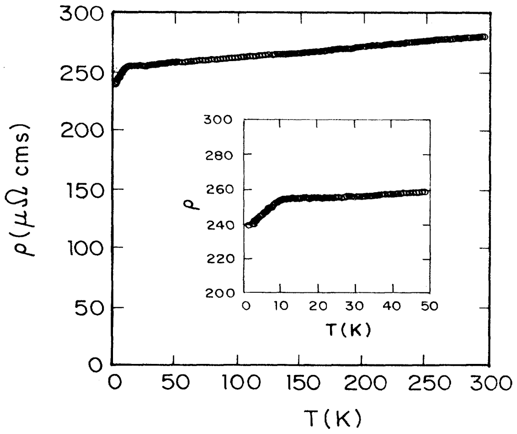

FIG. 5. Resistivity of $SmRuSn_3$.

To conclude, we have reinvestigated the magnetic and transport properties of $SmRuSn_3$ and an analysis of our data, which takes into consideration the fact that the crystal structure has two inequivalent Sm sites, does *not* provide us with any compelling evidence to conclude that *all* the Sm ions are in a valence-fluctuating state as claimed earlier by Fukuhara, Sakamoto, and Sato.[1] Instead, we find that a description of the system as consisting of a static mixture of Sm ions with site-dependent properties is adequate. According to our analysis, Sm ions at 6*d* sites, which comprise 75% of the total population, are in the trivalent state and order magnetically at around 6 K. The remaining Sm ions at the 2*a* site are either divalent or weakly valence fluctuating. Some amount of atomic disorder involving Sm ions at the 2*a* site cannot be ruled out.

## ACKNOWLEDGMENT

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