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# Single Crystal Growth and Magnetic Properties of $SmCu_2Ge_2$

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We have succeeded in growing a single crystal of tetragonal $SmCu_2Ge_2$ in Sn-flux and measured the x-ray diffraction and magnetic susceptibility. The volume of the unit-cell and the magnetic behavior are consistent with trivalent Sm in $SmCu_2Ge_2$. It was confirmed that the temperature independent Van Vleck term arising from the $J = 7/2$ first excited state gives a large contribution to the magnetic susceptibility in $SmCu_2Ge_2$ similar to other Sm compounds. The difference in energy between the $J$=5/2 and 7/2 angular momentum states is roughly estimated to be $\Delta E \sim 1800$ K from the magnetic susceptibility.

**KEYWORDS:** $SmCu_2Ge_2$, single crystal growth, magnetic susceptibility

## 1. Introduction

Most $RT_2X_2$ (R: rare earth and actinide, T: transition metal, X: Si and Ge) compounds crystallize in the $ThCr_2Si_2$-type tetragonal structure (Fig. 1). The Ce, Yb and U intermetallic compounds with this crystal structure exhibit a variety of characteristic features including magnetic ordering, heavy fermion behavior, valence fluctuations and anisotropic superconductivity. Most such compounds investigated have been polycrystalline or low quality single crystals. Therefore, the details of physical properties are still unclear. In the case of $SmCu_2Ge_2$, only the lattice parameter has been reported. According to this previous report [1], the unit cell volume of $RCu_2Ge_2$ (R: rare earth) varies smoothly with rare earth even at Sm. This fact indicates that the valence of Sm would be close to $Sm^{3+}$ and a magnetic ground state can be expected. Recently, we succeeded to grow a single crystal of $SmCu_2Ge_2$ using the Sn-flux method. In order to clarify the ground state and the valence of Sm of this system, we measured the physical properties using single crystals. In this paper, we report the structural parameters and magnetic properties of $SmCu_2Ge_2$ in detail.

## 2. Experimental

Single crystals of $SmCu_2Ge_2$ were grown by the Sn-flux method. The starting materials were 3N(99.9% pure)-Sm, 5N-Cu, 5N-Ge, and 5N-Sn. These materials were put in an alumina crucible and sealed in a quartz tube with an off-stoichiometric composition of R:Cu:Si:Sn = 1:5:3:40. The ampoule was heated up to 1050 °C, maintained at this temperature for three days, and cooled to 500 °C at a rate of 1.5 °C/h, taking about 19 days in total. The excess flux was removed from the crystals by spinning the ampoule in the centrifuge. Figure 2 shows a typical single crystal sample with $4\times3\times1.5\,mm^3$. The flat plane corresponds to the (001) plane. We checked the elemental composition of the single crystal sample using the electron-probe microanalysis (EPMA) as Sm:Cu:Ge=1:2:2. X-ray measure-

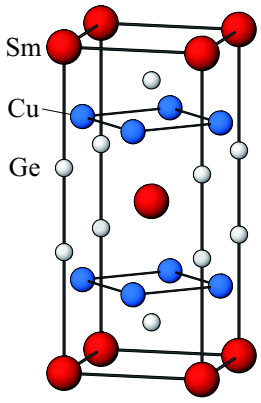


**Fig. 1.** (Color online) $ThCr_2Si_2$-type crystal structure in $SmCu_2Ge_2$.

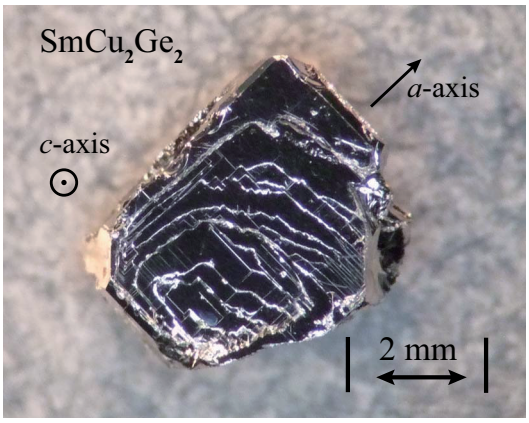


**Fig. 2.** (Color online) Typical single crystal of $SmCu_2Ge_2$.

ments were performed using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K$\alpha$ radiation. We selected a small high quality single crystal with dimensions of $0.07\times0.05\times0.04\,mm^3$ in order to minimize the absorption as well as the secondary extinction effects, which generally make the structural determination difficult. The single crystal sample of $SmCu_2Ge_2$ was mounted on a glass fiber. The magnetic susceptibility measurements were performed using a commercial SQUID magnetometer(Quantum Design MPMS-5). Crystallographical parameters were refined using SHELXL [2].

## 3. Results and Discussion

The structural parameters were refined by the analyses of the integrated intensities corrected for absorption and secondary extinction effects, as summarized in Table I. These lattice parameters are slightly larger than those reported data previously [1].

**Table I.** Atomic coordinates and thermal parameters of $SmCu_2Ge_2$ at 300 K from x-ray measurements. $R$ and $wR$ are the reliability factors and $B$ is the equivalent isotropic atomic displacement parameter.

| | atom | position | | | $B$ (Å$^2$) |
|---|---|---|---|---|---|
| $I4/mmm$(♯139) | (site) | $x$ | $y$ | $z$ | |
| $a$ = 4.0967(2) Å | Sm (2$a$) | 0 | 0 | 0 | 0.37(3) |
| $c$ = 10.2503(8) Å | Cu (4$d$) | 0 | 1/2 | 1/4 | 0.65(3) |
| $V$ = 172.032(20) Å$^3$ | Ge (4$e$) | 0 | 0 | 0.37973(10) | 0.41(3) |
| ($R$= 2.78%, $wR$= 6.18%) | | | | | |

Figure 3 shows the temperature dependence of magnetic susceptibility of $SmCu_2Ge_2$ for field along the $a-$ and $c$-axes. The overall behaviors are very similar to those of $SmCu_2Si_2$ except for the ordering temperature [3]. Around 15 K, the susceptibility shows a clear kink($a-$axis) and cusp($c-$axis), which corresponds to an antiferromagnetic ordering. This ordering temperature is higher than that of $SmCu_2Si_2$ ($T_N$ = 12 K) [3]. Generally, replacement of Si by Ge atom in $f$-electrons system is recognized as an application of negative chemical pressure because of the larger size of Ge atom. Hence there is expected a suppression of magnetic ordering in Sm-based compounds based only on size under the simple assumption of Doniach phase diagram [4]. However, it needs further clarification as

the simple interpretation can not be applicable for the $SmCu_2X_2$ system.

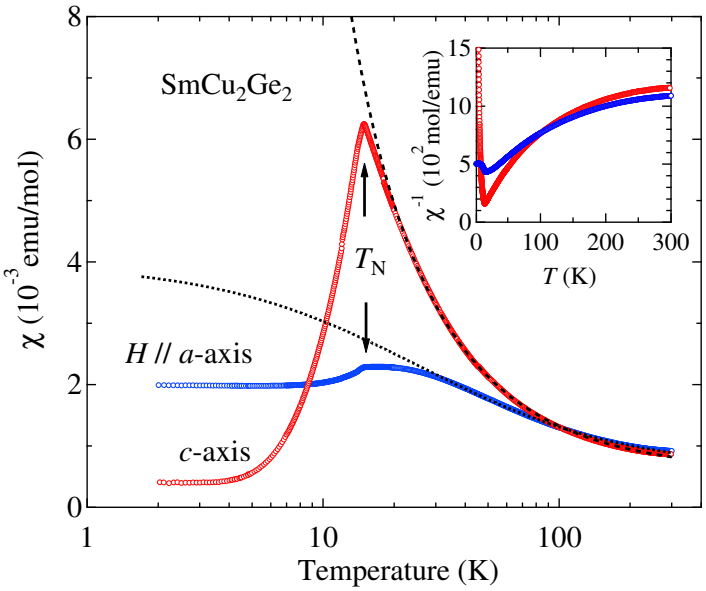


**Fig. 3.** (Color online) Temperature dependence of magnetic susceptibilities for field along $a-$ and $c-$axis, respectively. Inset show the reciprocal susceptibility.

Inset of Fig. 3 shows a plot of the reciprocal magnetic susceptibility for $SmCu_2Ge_2$. The behavior can not be described by a simple Curie-Weiss law, which is consistent with the $Sm^{3+}$ ions having relatively low-energy first excited states above the Hund's rule ground state. Furthermore, the magnetic susceptibility is isotropic at high temperatures. These facts make a determination of crystalline electric field (CEF) level scheme of $J$=5/2 ground state in $SmCu_2Ge_2$ difficult. Therefore, here we refer to the analysis of the magnetic susceptibility of $SmRh_4B_4$ and $SmCu_2Si_2$ at high temperatures [3, 5]. The magnetic susceptibility for Sm compounds can be often well described by the following formula:

$$\chi = N_{\rm A}\left(\frac{\mu_{\rm eff}^2}{3k_{\rm B}(T-\theta_{\rm p})} + \frac{20\mu_{\rm B}^2}{7\Delta E}\right) \quad , \tag{1}$$

where $N_{\rm A}$ is Avogadro's number, $k_{\rm B}$ is Boltzmann's constant, $\mu_{\rm B}$ is the Bohr magneton, $\mu_{\rm eff}$ is the effective magnetic moment, and $\theta_{\rm p}$ is the Curie-Weiss temperature [5, 6]. The first term represents a Curie-Weiss contribution from $J$ =5/2 ground state, while the second term is the temperature independent Van Vleck correction arising from the accessible first excited angular momentum $J$ = 7/2 state. In the absence of CEF, $\mu_{\rm eff} = g_J\sqrt{J(J+1)}\mu_{\rm B}$ is $0.845\mu_{\rm B}$, where $g_J$ is the Landé $g-$factor, and $\Delta E$ is the difference in energy between the $J$ = 5/2 and $J$ =7/2 angular momentum states. The best fits of formula (1) to the data of $H//a-$ and $c$-axis above 25 K are shown in Fig. 3 by broken lines, respectively. These lines are well described $\chi(T)$ of $SmCu_2Ge_2$ at high temperatures. The fitting parameters are $\mu_{\rm eff}$ = 0.83 $\mu_{\rm B}$ , $\theta_p$=-25.7 K, and $\Delta E$ = 1700 K for $a-$axis and $\mu_{\rm eff}$ = 0.76 $\mu_{\rm B}$ , $\theta_p$=3.5 K, and $\Delta E$ = 1860 K for $c-$axis. The determined effective moments are close to the theoretical values of 0.845 for free $Sm^{3+}$ ion. The values of $\Delta E$ for both field directions are roughly in good agreement with each other and with $\sim$ 1500 K estimated for free $Sm^{3+}$ [7].

## 4. Summary

We have succeeded in growing a single crystal of $SmCu_2Ge_2$ with the tetragonal structure by the Sn-flux method and measured the x-ray diffraction and magnetic susceptibility. The volume of the unit-cell and the magnetic behavior are consistent with that the valence of Sm in $SmCu_2Ge_2$ is $Sm^{3+}$. It was confirmed that the temperature independent Van Vleck term arising from the first excited multiplet $J = 7/2$ gives a large contribution to the temperature dependent magnetic susceptibility of $SmCu_2Ge_2$ similar to that seen in other Sm compounds. The difference in energy between the $J$=5/2 and 7/2 states is roughly estimated to be $\Delta E \sim 1800$ K from the magnetic susceptibility.

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### References

[1] W. Rieger and E. Parthé: Monatsh. Chem. **100** (1969) 444.
[2] G. M. Sheldick: Acta Cryst. **A64** (2008) 112.
[3] N. D. Dung, Y. Ota, K. Sugiyama, T. D. Matsuda, Y. Haga, K. Kindo, M. Hagiwara, T. Takeuchi, R. Settai, and Y. ŌnukiI: J. Phys. Soc. Jpn. **78** (2009) 024712.
[4] S. Doniach, in *Valence Instabilities and Related Narrow Band Phenomena*, ed. R. D. Parks (Plenum, New York, 1977).
[5] H. C. Hamaker, L. D. Woolf, H. B. Mackay, Z. Fisk, and M. B. Maple: Solid State Commun. **32** (1979) 289.
[6] for example, D. Wagner, *Introduction to the Theory of Magnetism*, (Pergamon Press, 1972) pp. 94-99.
[7] J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, (Oxford Press, 1932) 245-256.