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Magnetic properties of Heusler compounds Ru_2CrGe and Ru_2CrSn

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We have succeeded in synthesizing the Heusler compounds Ru_2CrGe and Ru_2CrSn and performed magnetization measurements in high magnetic fields up to 18 T in order to investigate the magnetic properties of Ru_2CrGe and Ru_2CrSn . We confirmed that the compounds have an ordered Heusler $L2_1$ structure. It was found that Ru_2CrGe is an antiferromagnet with the Néel temperature $T_N=13$ K and Ru_2CrSn shows a spin-glass-like behavior below 7 K. The Heisenberg exchange constants determined on the basis of the experimental results for Ru_2CrGe are different from the values of Mn-based Heusler compounds. © 2008 American Institute of Physics.

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Recently, Heusler compounds have attracted renewed interest because they have been expected to be candidates for future applications. Especially, half-metals attract a great deal of attention in spintronic applications. Since de Groot *et al.* reported the first theoretical prediction on the half-metallicity of NiMnSb and PtMnSb, called half-Heusler compounds, which have a $C1_b$ -type structure with XYZ composition (X and Y =transition metals, Z =*sp* elements),¹ many investigations on the half-metallicity of Heusler compounds have been performed experimentally and theoretically.²⁻⁵ Quite recently, Ishida *et al.*⁶ and Mizutani *et al.*⁷ performed band structure calculations on Cr-based Heusler compounds having an $L2_1$ -type structure with X_2YZ composition, the so-called full-Heusler compounds, and reported that Fe_2CrZ (Z =Si and Ge) and $(\text{Ru}_{1-x}\text{Fe}_x)_2\text{CrSi}$ are complete or nearly complete half-metals and the predicted saturation magnetic moments of these alloys are $2\mu_B$ in a wide range of Fe concentration. However, the experimental results for $(\text{Ru}_{1-x}\text{Fe}_x)_2\text{CrSi}$ and $(\text{Ru}_{1-x}\text{Fe}_x)_2\text{CrGe}$ show that the saturation magnetization and Curie temperature decrease with increasing Ru concentration.⁸⁻¹⁰ So far, the experimental results of the end compounds, Fe_2CrZ and Ru_2CrZ , have not been reported. We have tried to synthesize Cr-based Heusler compounds containing Fe and Ru in order to understand the magnetic properties of these alloys and compounds. In this study, we have succeeded in synthesizing Heusler compounds Ru_2CrGe and Ru_2CrSn and performed magnetization measurements in high magnetic fields up to 18 T.

Polycrystalline samples of Ru_2CrGe and Ru_2CrSn were prepared by arc melting the stoichiometric mixture of the high-purity constituent elements in an argon atmosphere. The ingots were annealed in an evacuated quartz tube at 1273 K for 5 days and finally quenched in water. Powder x-ray diffraction experiments with Cu $K\alpha$ radiation were performed at room temperature. The observed diffraction patterns were analyzed in comparison with calculated patterns using a Rietveld program (RIETAN).¹¹ The magnetizations in magnetic fields $B \leq 7$ T were measured by a superconducting quantum

interference device (SQUID) magnetometer (Quantum Design). The high field magnetizations up to 18 T were obtained using a sample-extraction magnetometer.¹²

Figure 1 shows the observed and calculated powder x-ray diffraction patterns of Ru_2CrGe and Ru_2CrSn at room temperature. All the maxima can be indexed on the basis of the space group $Fm\bar{3}m$. We observed the (111) and (200) reflections, which are related to an atomic order in the $L2_1$ structure. The observed intensities agree with the results calculated as the Heusler $L2_1$ structure. Therefore, the samples obtained in this study are single phase of the ordered Heusler $L2_1$ structure. The lattice constants at room temperature are estimated to be 0.5971 and 0.6195 nm for Ru_2CrGe and Ru_2CrSn , respectively.

Figure 2 shows the temperature dependence of the magnetic susceptibility of Ru_2CrGe at magnetic field of 0.01 T. A distinct peak was observed at 13 K, indicating an antiferromagnetic transition at $T_N=13$ K. The peak becomes broad and shifts to temperature higher than $T_N=13$ K by applying higher magnetic fields, as shown in the inset of Fig. 1. In the paramagnetic region, we fitted the data points in the tempera-

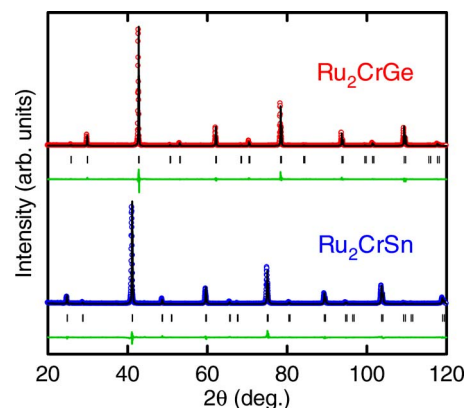


FIG. 1. (Color online) The observed (open circles) and calculated (solid lines) powder x-ray diffraction patterns of Ru_2CrGe and Ru_2CrSn at room temperature. The different patterns are shown below the data. The vertical lines show the Bragg peak positions for the Heusler $L2_1$ structure. The R factors were $R_{\text{wp}}=16.6\%$ and $R_f=4.5\%$ for Ru_2CrGe and $R_{\text{wp}}=17.8\%$ and $R_f=4.3\%$ for Ru_2CrSn .

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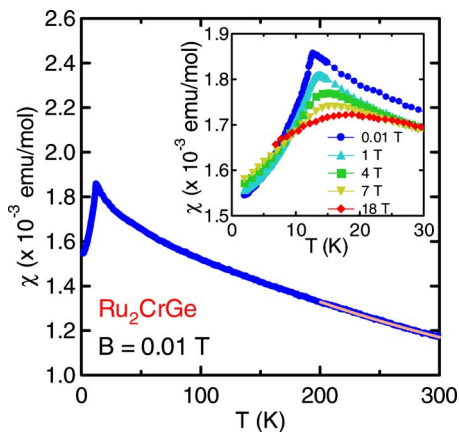


FIG. 2. (Color online) Temperature dependence of the magnetic susceptibility of Ru_2CrGe at 0.01 T. The solid curve represents the fit by the Curie–Weiss law containing the temperature-independent term. The inset shows the temperature dependence of the magnetic susceptibility below 30 K at various magnetic fields up to 18 T.

ture range of 200–300 K by the Curie–Weiss law containing a temperature-independent term, $\chi(T) = \chi_0 + C/(T - \theta_{\text{CW}})$. Here, χ_0 , C , and θ_{CW} denote the temperature-independent term, Curie constant, and Curie–Weiss temperature, respectively. The obtained values of χ_0 and θ_{CW} and the effective number of Bohr magneton p_{eff} evaluated from the Curie constant are 1.34×10^{-4} emu/mol, -453 K, and $2.50\mu_B$, respectively. The paramagnetic moment, $p_c = \sqrt{1 + p_{\text{eff}}^2} - 1$, is estimated to be $1.69\mu_B/\text{f.u.}$

Figure 3 shows the temperature dependence of the magnetic susceptibility of Ru_2CrSn at magnetic field of 0.01 T. The magnetic susceptibility exhibits a peak at 7 K. We observed a difference in the magnetic susceptibility curves between the zero-field-cooling (ZFC) and field-cooling (FC) processes, suggesting a spin glass transition at $T_g = 7$ K, as shown in the inset of Fig. 3. However, the difference begins to appear below 60 K. From the fitting procedure in the paramagnetic region mentioned above, χ_0 , θ_{CW} , p_{eff} , and p_c are estimated to be 6.24×10^{-4} emu/mol, -193 K, $1.34\mu_B/\text{f.u.}$, and $0.67\mu_B/\text{f.u.}$, respectively. Figure 4 shows the magnetization curves of Ru_2CrSn at 2, 30, and 100 K. The magnetization increases linearly at 2, 30, and 100 K with increasing

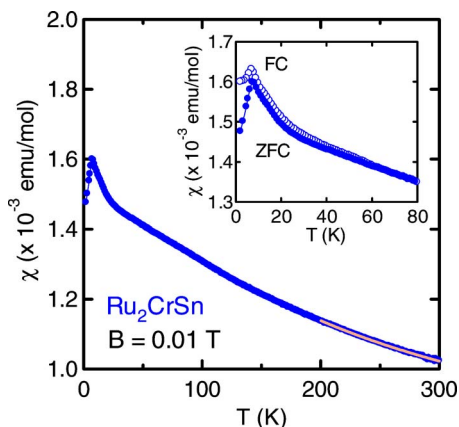


FIG. 3. (Color online) Temperature dependence of the magnetic susceptibility of Ru_2CrSn at 0.01 T in the ZFC process. The solid curve represents the fit by the Curie–Weiss law containing the temperature-independent term. The inset shows the temperature dependence of the magnetic susceptibility below 80 K at 0.01 T in the ZFC and the FC processes.

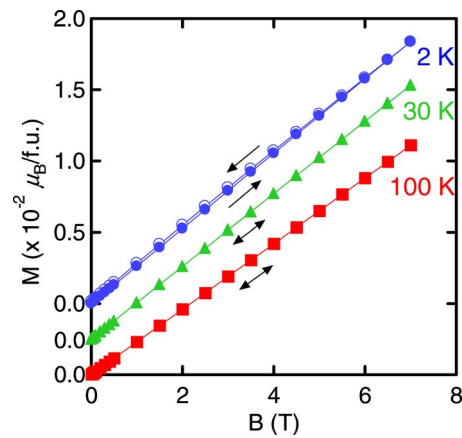


FIG. 4. (Color online) Magnetization curves of Ru_2CrSn at 2, 30, and 100 K in the magnetic field increasing (solid symbols) and decreasing (open symbols) processes. The arrows indicate the magnetization processes with increasing and decreasing magnetic fields.

magnetic field. In the magnetic field decreasing process, the magnetization at 2 K is slightly larger than that in the magnetic field increasing process, whereas the magnetization processes at 30, and 100 K are reversible. Therefore, it is considered that Ru_2CrSn shows the spin glass state below 7 K.

In this study, we have succeeded in synthesizing the Heusler compounds Ru_2CrGe and Ru_2CrSn and found that Ru_2CrGe is an antiferromagnet with $T_N = 13$ K and Ru_2CrSn shows spin-glass-like behavior below 7 K. The results of recent neutron diffraction measurements carried out on Ru_2CrGe indicate that Ru_2CrGe has an antiferromagnetic type-2 (AM2) structure.¹³ The structure is composed of ferromagnetically aligned (111) planes with adjacent (111) planes coupled antiferromagnetically. The magnetic moment of $p_s = 1.45\mu_B$ at 5 K is confined to the Cr atoms with the direction being perpendicular to the propagation vector. We observed that the magnetic susceptibility of Ru_2CrGe shows the distinct peak indicating the antiferromagnetic transition at $T_N = 13$ K. However, the peak shifts to the higher temperature side by applying high magnetic fields. The origin of the magnetic field effect for T_N is not clear. The spin-glass-like behavior of Ru_2CrSn may be attributed to the competition of the magnetic correlation or to the magnetic frustration induced by the replacement of Ge by Sn. On the other hand, Heusler compounds are known to suffer from chemical disorders of the constituent elements.^{6,7,14–17} Although we confirmed that Ru_2CrGe and Ru_2CrSn have the $L2_1$ structure, a slight chemical disorder may lead to the spin-glass-like behavior and the small difference between the ZFC and the FC processes below 60 K in Ru_2CrSn .

Most Heusler compounds have been considered to be local-moment ferromagnets. Hence, Ru_2CrGe is a rare Heusler compound with antiferromagnetic transition. So far, the AM2 structure in Heusler compounds has been found in Ru_2MnZ ($Z = \text{Ge}, \text{Sn}, \text{and Sb}$) and Pd_2MnIn .^{18–23} According to previous reports on Mn-based Heusler compounds, the magnetic moments of Mn atoms are considered to be coupled by an indirect exchange interaction via conduction electrons because the Mn atoms have localized magnetic moments of $\sim 4\mu_B$ per Mn atom and the nearest neighbor Mn atoms are separated by ~ 0.4 nm. In Ru_2CrZ ($Z = \text{Ge}$ and Sn), the nearest neighbor Cr–Cr distances are 0.4222 and

0.4381 nm for Ru₂CrGe and Ru₂CrSn, respectively. From the magnetic moment p_s observed by the neutron diffraction measurements and from the paramagnetic moment p_c , the Rhodes–Wohlfarth ratio p_c/p_s of Ru₂CrGe is estimated to be 1.17, which is close to $p_c/p_s=1$ expected for local-moment magnets. However, Ru₂CrGe has low Néel temperature and small Cr magnetic moment compared with those of Mn-based AM2 Heusler compounds. Moreover, the Heisenberg exchange constants of the nearest and the next nearest neighbor interactions, J_1 and J_2 , estimated from θ_{CW} and T_N for Ru₂CrGe are -35 and -2.1 K, respectively, whereas those of the Mn-based AM2 compounds show $J_1 > 0$, $J_2 < 0$, and $|J_2| > J_1$,^{19–23} indicating that Mn–Mn interactions have an oscillating nature and the compounds are in the AM2 region of the grand state phase diagram obtained by Morán-López *et al.*²³ These results suggest that the mechanism of the magnetic interaction in Ru₂CrGe is different from that in Mn-based Heusler compounds and is beyond the mean field theory.

In summary, we have succeeded in synthesizing Ru₂CrGe and Ru₂CrSn and investigated the magnetic properties of the compounds. We found that Ru₂CrGe is antiferromagnetic at $T_N=13$ K and Ru₂CrSn shows spin-glass-like behavior below 7 K. The magnetic properties of Ru₂CrGe are different from those of Mn-based antiferromagnetic Heusler compounds, suggesting that the mechanism of the magnetic interaction is different from that in local-moment magnets within the mean field theory.

The magnetization measurements using a SQUID magnetometer were carried out at the Center for Low Temperature Science, Tohoku University. The high field magnetization measurements were performed at the HFLSM, IMR, Tohoku University. H.O. is grateful for the JPSJ Research Fellowships for Young Scientists.

- ¹R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, *Phys. Rev. Lett.* **50**, 2024 (1983).
- ²S. Ishida, *Advances in Condensed Matter and Materials Research* (Nova Science, New York, 2003), Vol. 4, pp. 149–178.
- ³K. Inomata, S. Okamura, R. Goto, and N. Tezuka, *Jpn. J. Appl. Phys., Part 2* **42**, L419 (2003).
- ⁴T. Block, C. Felser, G. Jakob, J. Ensling, B. Mühling, P. Gütling, and R. J. Cava, *J. Solid State Chem.* **176**, 646 (2003).
- ⁵Y. Sakuraba, T. Miyakoshi, M. Oogane, Y. Ando, A. Sakuma, T. Miyazaki, and H. Kubota, *Appl. Phys. Lett.* **89**, 052508 (2006).
- ⁶S. Ishida, S. Mizutani, S. Fujii, and S. Asano, *Mater. Trans.* **47**, 31 (2006).
- ⁷S. Mizutani, S. Ishida, S. Fujii, and S. Asano, *Mater. Trans.* **47**, 25 (2006).
- ⁸K. Matsuda, M. Hiroi, and M. Kawakami, *J. Phys.: Condens. Matter* **17**, 5889 (2005).
- ⁹M. Hiroi, K. Matsuda, and T. Rokkaku, *Phys. Rev. B* **76**, 132401 (2007).
- ¹⁰Y. Kusakari, T. Kanomata, K. Fukushima, and H. Nishihara, *J. Magn. Magn. Mater.* **310**, e607 (2007).
- ¹¹F. Izumi, *The Rietveld Method* (Oxford University, Oxford, 1993), p. 236.
- ¹²K. Koyama, S. Miura, H. Okada, and K. Watanabe, *J. Phys.: Conf. Ser.* **51**, 569 (2006).
- ¹³K. R. A. Ziebeck, personal communication (March 27, 2007).
- ¹⁴M. P. Raphael, B. Ravel, Q. Huang, M. A. Willard, S. F. Cheng, B. N. Das, R. M. Stroud, K. M. Bussmann, J. H. Claassen, and V. G. Harris, *Phys. Rev. B* **66**, 104429 (2002).
- ¹⁵B. Ravel, M. P. Raphael, V. G. Harris, and Q. Huang, *Phys. Rev. B* **65**, 184431 (2002).
- ¹⁶S. Picozzi, A. Continenza, and A. J. Freeman, *Phys. Rev. B* **69**, 094423 (2004).
- ¹⁷Y. Miura, K. Nagao, and M. Shirai, *Phys. Rev. B* **69**, 144414 (2004).
- ¹⁸M. Gotoh, M. Ohashi, T. Kanomata, and Y. Yamaguchi, *Physica B* **213–214**, 306 (1995).
- ¹⁹S. Ishida, S. Kashiwagi, S. Fujii, and S. Asano, *Physica B* **210**, 140 (1995).
- ²⁰T. Kanomata, M. Kikuchi, and H. Yamauchi, *J. Alloys Compd.* **414**, 1 (2006).
- ²¹J. Kübler, A. R. Williams, and C. B. Sommers, *Phys. Rev. B* **28**, 1745 (1983).
- ²²P. J. Webster and R. S. Tebble, *J. Appl. Phys.* **39**, 471 (1968).
- ²³J. L. Morán-López, R. Rodríguez-Alba, and F. Aguilera-Granja, *J. Magn. Magn. Mater.* **131**, 417 (1994).