Appearance of Ferromagnetism in Heusler alloy Ru$_2$Mn$_{1-x}$V$_x$Ge

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Abstract

The crystallographic and magnetic properties of the quaternary Heusler alloys Ru$_2$Mn$_{1-x}$V$_x$Ge were investigated. Although the end members, Ru$_2$MnGe ($x = 0$) and Ru$_2$VGe ($x = 1$), are antiferromagnetic and paramagnetic, ferromagnetism with Curie temperature over 200 K appeared at about $x = 0.3$. The saturation magnetization had a maximum ($1.6\mu_B$/f.u.) at $x = 0.5$. The ferromagnetism was explained by a model which assumes a preferential site occupation of V atoms and a collapsing of the next nearest-neighbor antiferromagnetic Mn-Mn interactions by V.
**Introduction**

Half-metallic ferromagnets (HMFs) have attracted a scientific and technological interest because HMFs are expected to be a key material for ferromagnetic electrode in the spintronics devices [1, 2]. From this standpoint, $X_2YZ$-type Heusler alloys have attracted much attention because some of them were predicted to be HMF [3, 4]. In these alloys, $X$ and $Y$ are the 3$d$, 4$d$, or 5$d$ transition metal element, and $Z$ is a III–V group element. It is suggested for Heusler alloys that their magnetic or electronic properties have a close relationship with the number of the valence electron [5-7].

Among the $X_2YZ$-type Heusler alloys, the manganese Heusler alloy systems of $X_2MnZ$ have attracted attention because most of these are ferromagnetically ordered with a magnetic moment of $\sim 4\mu_B$/Mn [8]. A neutron diffraction study for the ferromagnetic Heusler alloys $X_2MnZ$ ($X=\text{Pd, Ni}; Z=\text{Sn, Al}$) revealed that the magnetic interactions are long-range [9, 10]. Moreover, a band-theoretical study for $X_2MnZ$ indicated that the electron levels in the vicinity of the Fermi level plays an important role in the formation of a magnetic moment and determine the type of the magnetic order [11, 12]. The conduction electron density and the $p$-$d$ state hybridization of nonmagnetic atom and Mn atom seem to play an important role in the magnetic properties of the manganese Heusler alloys $X_2MnZ$. Therefore, it seems very interesting to study the substitution effect of nonmagnetic atoms on the magnetic and transport properties of the $X_2MnZ$ system. From these viewpoints we focused on Ru$_2$MnGe. In regard to Ru$_2$MnGe, Gotoh *et al.* and Kanomata *et al.* revealed from a neutron diffraction, x-ray and magnetic measurements that it has a type-II antiferromagnet order and only Mn carries a magnetic moment of $3.2 \sim 3.8 \mu_B$ [13, 14].

In this study, we prepared polycrystalline samples of the Ru$_2$Mn$_{1-x}$V$_x$Ge system
and investigated the substitution effect of nonmagnetic V on the crystallographic and magnetic properties of Ru$_2$MnGe. This paper reports the results of crystallographic and magnetic analyses performed for the Ru$_2$Mn$_{1-x}$V$_x$Ge system, and the cause of the ferromagnetism is also discussed.

**Experiment**

Polycrystalline samples of Ru$_2$Mn$_{1-x}$V$_x$Ge (0 ≤ x ≤ 1) were prepared by arc melting of stoichiometric amounts of the raw materials in a zirconium-gettered Ar atmosphere. The polycrystalline ingots were annealed in an evacuated quartz ampoule at 1173 K for 3 days and then quenched in water. The crystal structure was refined by the Rietveld analysis for the x-ray powder diffraction (XRD) data obtained at room temperature using Cu-Kα radiation. The magnetic properties were measured using a SQUID magnetometer.

**Results and discussion**

It was found that vanadium can be substituted up to x = 1.0 in the Ru$_2$Mn$_{1-x}$V$_x$Ge system. The XRD profiles for Ru$_2$Mn$_{1-x}$V$_x$Ge (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) are shown in Fig.1 (a). The result of the refinement for the XRD data indicates that all the samples are composed of a single phase and all the peaks in the profile can be indexed as a full Heusler $L_2^1$ cubic structure. Figure 1(b) shows the lattice parameter as a function of the V content. The cubic lattice parameter $a$ is almost constant for samples with a V content between x =0 and 1.0. The value of the lattice parameter for x = 0 Ru$_2$MnGe is consistent with those reported in former studies within experimental error [9]. Since the metallic radius of V (0.135 nm) is close to that of Mn (0.127 nm), no
remarkable change would be observed in the V-content dependence of the lattice constant.

Figure 2(a) and 2(b) show the temperature dependence of the magnetization measured for samples with various V compositions \((0 \leq x \leq 1)\) under an applied field of 0.1 T. The samples of \(x = 0\) and 0.2 were antiferromagnetic, whereas samples of \(0.3 \leq x \leq 0.6\) were ferromagnetic with Curie temperature \(T_C\) of \(160 \sim 200\) K. When the V content exceeded \(x = 0.6\), \(T_C\) decreases remarkably by presumably suppression of the ferromagnetism. The magnetization of \(\text{Ru}_2\text{VGe} (x = 1)\) shows paramagnetic temperature dependence.

The Néel temperature \(T_N\), Curie temperature \(T_C\), and Curie-Weiss temperature \(\Theta\), which were determined from the magnetization data, are shown in Fig.3 (a) and 3 (b) as a function of the V content \(x\). \(\Theta\) shows a slight increase for samples of \(0 \leq x \leq 0.2\); however, it shows an abrupt increase at a composition of \(0.2 < x < 0.3\). \(\Theta\) shows a monotonous increase from \(x = 0.3\) to 0.5, and, after having a maximum at \(x = 0.5\), it decreases as the V content increases. Since \(\Theta\) coincides well with \(T_C\) at a composition of \(0.3 \leq x \leq 0.6\), a typical ferromagnetic state seems to be established at these compositions. A sample of \(x = 0.5\) has the highest \(T_C\). \(T_C\) shows a small V content dependence at \(0.3 \leq x \leq 0.6\); however, it decreases remarkably as the V content increases over \(x = 0.6\).

Figure 4(a) and 4(b) show the field dependence of the magnetization for \(\text{Ru}_2\text{Mn}_{1-x}\text{V}_x\text{Ge} (0 \leq x \leq 1)\) at 5 K. The magnetization of \(x = 0\) and 1 shows almost linear field dependence. These results and the temperature dependence of the magnetization indicate that the sample \(x = 0\) is antiferromagnetic and the sample \(x = 1\) is paramagnetic at 5 K. On the other hand, although the thermomagnetic curve of sample
\( x = 0.2 \) shows antiferromagnetic behavior, the magnetization at 5 K shows magnetic hysteresis at lower fields; however, it persists to increase linearly at higher magnetic fields. The magnetization curves of other samples show typical ferromagnetic behavior with a characteristic of soft magnetic materials and tend to be saturated above 0.2 T.

Figure 5 shows the V-content dependence of the magnetization obtained under an applied field of 1 T at 5 K. The magnetization increased remarkably at about \( x = 0.3 \) and continued to increase; however, after reaching a maximum at \( x = 0.5 \) it tends to decrease up to \( x = 1 \) (Ru2VGe). The magnetization for \( x = 0.5 \) was about 1.6 \( \mu_B/\text{f.u.} \).

As mentioned above, neutron diffraction studies for Ru2MnGe revealed that Mn has a moment of 3.8 \( \mu_B \) and only Mn carries a magnetic moment [13]. When we assume the moment 3.8 \( \mu_B/\text{Mn} \), 1.9 \( \mu_B/\text{f.u.} \) is assigned for Ru2Mn0.5V0.5Ge. Furthermore, 2 \( \mu_B \) is estimated by the Slater-Pauling rule for the alloy with 26 valence electrons. The present experimental value of 1.6 \( \mu_B/\text{f.u.} \) seems consistent with these values.

According to these results, we discuss the mechanism of induction of ferromagnetism by the model based on the proposal of Kanomata et al. (hereafter referred to as Kanomata’s model) [14]. Kanomata’s model focuses on the localized character observed for Ru2MnGe and takes account of the ferromagnetic interaction \( J_1 \) and the antiferromagnetic interaction \( J_2 \) between Mn atoms, which are shown in Fig.6. In the samples of \( x \leq 0.2 \), V seems to replace the Mn site randomly. As a result, one V atom collapses twelve \( J_1 \) interactions and six \( J_2 \) interactions. Kanomata et al. estimated the magnitudes of the \( J_1 \) and \( J_2 \) interaction as 5.6 and -13.2 K, respectively. Therefore, no remarkable change in the V-content dependence of \( \Theta \) (fig. 4) would be suggested that the magnitudes of the \( J_1 \) and \( J_2 \) interaction would be same in the samples.
of \( x \leq 0.2 \). In the composition range of \( x = 0.2 \sim 0.3 \), \( \Theta \) shows an abrupt change for the V substitution. In general, \( T_N \) is determined through the competition of various magnetic interactions, and, therefore, it often shows discontinuous composition dependence when the substitution induces a change in the magnetic structure. On the other hand, since \( \Theta \) is a parameter that represents the response characteristics of the system to the applied field, it does not show discontinuous change if nothing happens in the crystal structure. Figure 1 shows no change in the crystal structure, therefore, the discontinuous change of \( \Theta \) requires another explanation.

Here, we propose a possible model by assuming a preferential site occupation of V atoms to explain the discontinuous change of \( \Theta \) and the appearance of ferromagnetism. The preferential occupation of the V atom would stabilize the energy of the system to ferromagnetic from antiferromagnetic states. When \( J_1 \) and \( J_2 \) of Kanomata’s model was introduced, the discontinuous change would be attributed to an abrupt decrease in the contribution of \( J_2 \), which makes a negative contribution to the \( \Theta \). If the V content increases over \( x = 0.2 \), the V atom would have a tendency to accumulate in the (111) planes. This cause a decrease in the interplaner antiferromagnetic interaction \( J_2 \) dominating the intraplaner ferromagnetic interaction \( J_1 \). At a composition of \( x = 0.5 \), (111) planes are alternately occupied by Mn or V atoms. In this case, V atoms cause the collapse of the interplaner exchange interactions \( J_2 \) between Mn atoms and ferromagnetism appears due to intraplaner ferromagnetic interaction \( J_1 \). When the V content increases over \( x = 0.5 \), V atoms start to invade the Mn plane, and, therefore, the magnetization and \( T_C \) decrease. This mechanism would induce the abrupt change of \( \Theta \) and generate ferromagnetism.
Conclusion

We found the appearance of ferromagnetism in the Heusler alloy system of Ru$_2$Mn$_{1-x}$V$_x$Ge. The end members of the system are antiferromagnetic (Ru$_2$MnGe) and paramagnetic (Ru$_2$VGe); however, ferromagnetism was observed for samples with intermediate V compositions. Ru$_2$Mn$_{0.5}$V$_{0.5}$Ge has a magnetic moment of 1.6 $\mu_B$/f.u.

The occurrence of ferromagnetism was explained by a model, which assumes a preferential site occupation of V atoms and the competition between the nearest-neighbor ferromagnetic and next nearest-neighbor antiferromagnetic interaction between Mn atoms. When V collapses antiferromagnetic interactions dominating ferromagnetic interaction, the system shows ferromagnetism.

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**Figure caption**

Fig. 1 (a) XRD profiles for the Ru$_2$Mn$_{1-x}$V$_x$Ge system and (b) the cubic lattice constant $a$ as a function of $x$.

Fig. 2 Temperature dependence of the magnetization under 0.1 T for the Ru$_2$Mn$_{1-x}$V$_x$Ge system. (a) shows the results for the samples of $x = 0$, 0.2, and 1 and (b) shows those of $x = 0.4$, 0.5, 0.6, and 0.8.

Fig. 3 (a) Néel temperature $T_N$ and Curie temperature $T_C$, and (b) Curie-Weiss temperature $\Theta$ as a function of V content $x$.

Fig. 4 Field dependence of the magnetization at 5K for the Ru$_2$Mn$_{1-x}$V$_x$Ge system. (a) shows the results for the samples of $x = 0$, 0.2, and 1 and (b) shows those of $x = 0.4$, 0.5, 0.6, and 0.8.

Fig. 5 V-content dependence of the magnetization at 5K determined at 1 T in the magnetization curve (line and markers) and the theoretical Slater Pauling curve (broken line) for the Ru$_2$Mn$_{1-x}$V$_x$Ge system.

Fig. 6 Possible magnetic interactions in the Ru$_2$MnGe crystal.
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Figure. 3 S. Mizusaki et al.
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