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# Crystal structure and magnetic properties of $DyCu_xGa_{2-x}$ ($x = 0$–$2.0$) antiferromagnetic compounds

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ABSTRACT

$DyCu_xGa_{2-x}$ ($x = 0$–$2.0$) compounds have been synthesized; meanwhile, their crystal structure and magnetic properties have been investigated by X-ray diffraction and magnetic measurements. The result shows that the continuous solid-solution series crystallize in three phases, with the structure types of $AlB_2$ ($x = 0$–$0.2$), DyCuGe ($x = 0.3$–$0.6$) and $CeCu_2$ ($x = 0.7$–$2.0$), respectively. The main reason to form the three structure types is considered to be the average atomic radius ratio of R to Cu/Ga. Magnetic-ordering transition of the compounds with $x = 0.2$–$0.6$ takes place at about 20 K and 113 K, while those of other compounds only takes place at about 20 K, which is attributed to the change of the near Dy–Dy distances and the ordered substitution of Ga by Cu.



## 1. Introduction

In the past years, several ternary intermetallic phases ($RT_xX_{2-x}$) formed by rare earth metals (R) with transition metals (T) and p-block elements (X) of the Periodic Table, have been studied for the structure and magnetic properties, however, the vast majority of papers focus on the RTX (1:1:1) or the $RT_{1.5}X_{0.5}$ compounds, including the ternary $RCu_{0.5}Ga_{1.5}$ systems which crystallize in $CaIn_2$-type structure [1–8,17]. The series of $RCu_2$ intermetallic compounds have the orthorhombic $CeCu_2$-type structure with antiferromagnetic (AFM) order at low temperatures [9,10]. It was found that $RCu_2$ compounds have a great magnetostrictive effect, and a significant second-order phase transition with a large magnetic entropy change around their Neel temperature [11,12]. The $RGa_2$ compounds crystallize in a simple layered hexagonal structure of the $AlB_2$-type and have a complex AFM order at low temperatures [13–15]. Due to the dramatic properties of the $DyCu_2$ and the $DyGa_2$ compounds, the $R(Cu,Ga)_2$ system may have noteworthy property, so these system need to be further studied.

In this paper, the effect of mutual substitution of Cu and Ga on the crystal structure and the magnetic property of the $DyCu_xGa_{2-x}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.7, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0) series were studied systematically.

## 2. Experimental details

The polycrystalline $Dy(Cu,Ga)_2$ samples were prepared by arc melting in a purified argon atmosphere, and approximately 5 wt.% excess rare earth was added during melting. The purity of the rare earth and the metals was 99.9% or better. Then the ingots were annealed in an evacuated and sealed silica tube at 700 or 1000 °C for 90 h for homogeneousness.

X-ray diffraction (XRD) measurements were carried out using X'pert Pro MPD diffractometer (Cu Kα radiation) with X'celerator detector, and the XRD patterns were refined using the HighScore Plus and Fullprof softwares. The *M–T* curves were measured by the magnetic property measurement system (MPMS-7, manufactured by Quantum Design Inc.) from 3 to 150 K with an applied field of 50 Oe.

## 3. Results and discussion

### 3.1. Crystal structure

The XRD patterns of the $DyCu_xGa_{2-x}$ ($x = 0$–$2.0$) compounds can be divided into three kinds, $x = 0$–$0.2$, $x = 0.3$–$0.6$, and $x = 0.7$–$2.0$. A comparison of three typical XRD patterns of the $DyCu_xGa_{2-x}$ ($x = 0$, 0.6, 2.0) is shown in Fig. 1. It can be seen that the position and relative intensity of the corresponding diffraction peaks of $DyCu_2$ are different from that of $x = 0$, 0.6, which indicates that they belong to different crystal structure types. The XRD pattern of $DyGa_2$ is similar to that of $x = 0.6$, however, there are some differences between them. Except that

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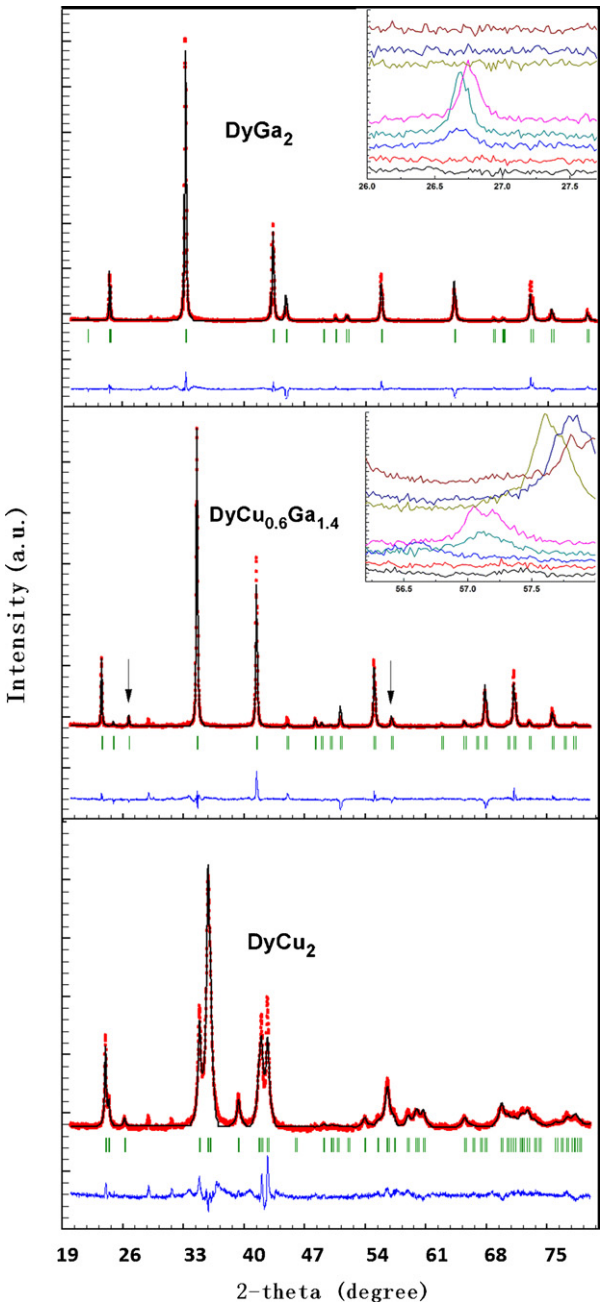


**Fig. 1.** The comparison of the XRD patterns of $DyCu_xGa_{2-x}$ ($x = 0, 0.6, 2.0$). The insets are the amplifying patterns of $DyCu_xGa_{2-x}$ ($x = 0, 0.2, 0.3, 0.4, 0.6, 0.7, 0.8, 1.0$, from bottom to top) around 27° and 57°.

the position and relative intensity of the corresponding diffraction peaks are of little different, two weak peaks around 27° and 57° (indicated by the arrows in Fig. 1) are observed in the pattern of $x = 0.6$, which differs from that of $DyGa_2$. In the amplified patterns of $DyCu_xGa_{2-x}$ ($x = 0, 0.2, 0.3, 0.4, 0.6, 0.7, 0.8, 1.0$) around 27° and 57° (see insets of Fig. 1), it can be seen that the patterns of $x = 0$, 0.2 do not have any peak, nevertheless, when $x$ increases from 0.3 to 0.6, the two peaks appear and gradually become stronger, then with the increase in $x$, the peaks disappear (when $x$ increases from 0.7 to 1.0, the patterns have a peak at 57.7° like $x = 0.6$, but it is not the same peak discussed above). This indicates that $DyCu_xGa_{2-x}$ ($x = 0.2$) has the same structure type as $RGa_2$, while the compounds of $x = 0.3, 0.4, 0.6$ crystallize in another structure type.

Comparing the diffraction patterns of ternary or any binary compounds composed of Dy, Cu and Ga in the powder diffraction database, it is found that the pattern of $x = 0.6$ is consistent with that of $DyCu_{0.36}Ga_{1.46}$ (ICCD reference pattern 00-054-0491), and it is thought by the author that the pattern is crystallized in $CaIn_2$-type structure (space group $P6_3/mmm$). By fitting the diffraction patterns using Rietveld method, it is determined that the compounds of $x = 0.2$–0.6 form a DyCuGe-type structure (space group $P6_3mc$). Furthermore, it is found by analysis that the only difference between the two structures is random occupation ($CaIn_2$-type, 4f sites) or ordered occupation (DyCuGe-type, the 4f sites are divided into two 2d sites) of the Cu and Ga atoms. The diffraction patterns of $x = 0.3$–0.6 show Cu and Ga atoms are ordered occupation, so the space group should be $P6_3mc$ instead of $P6_3/mmm$.

In summary, the structure of $DyCu_xGa_{2-x}$ series compounds can be divided into three kinds, $AlB_2$-type with $x = 0$–0.2, DyCuGe-type with $x = 0.3$–0.6 and $CeCu_2$-type with $x = 0.7$–2.0. The $AlB_2$-type structure belongs to hexagonal structure (space group P6/mmm), with Dy occupying the 1a (0, 0, 0) site and Ga occupying the 2d (1/3, 2/3, 1/2) sites. DyCuGe-type structure belongs to another hexagonal structure (space group $P6_3mc$), Dy occupies the 2a (0, 0, 1/4) sites, Ga occupies the 2b (1/3, 2/3, 1/2) sites, Cu and the remaining Ga occupies another 2b (1/3, 2/3, 0) sites. These two structures are typical layered structure, with Dy atom layer and Cu/Ga atom layer stacking alternately along the $c$ axis. $CeCu_2$-type structure belongs to orthorhombic structure (space group Imma), with Dy occupying the 4e (0, 1/4, z) sites ($z \approx 0.54$), Cu and Ga occupying the 8 h (0, $y$, $z$) sites ($y \approx 0.05$, $z \approx 0.16$).

In order to understand the relationship among the three types of structure, a comparison diagram of these three crystal structures has been plotted (Fig. 2). By comparing the projection of $AlB_2$-type structure with that of DyCuGe-type along the $c$ axis, it is found that they are very similar to each other. The only difference is that the substitution of Ga by Cu is no longer random ($x = 0$, 0.2), but preferential ($x = 0.3$–0.6) which makes the original 2d sites of $DyGa_2$ separate into two alternating 2b sites along the $c$ axis. However, the amount of Cu atoms is insufficient to completely occupy one of the two 2b sites. Besides, due to the separation of Ga sites in the $DyGa_2$ structure, the symmetry of the structure reduces. Thus the $DyCu_xGa_{2-x}$ ($x = 0.3$–0.6) compounds become a new hexagonal structure with the periodic length along the $c$ axis doubled.

As $x$ continually increases, the lattice gradually contracts due to the fact that the atomic radius of Cu is smaller than that of Ga. When $x$ is more than 0.6, Dy atoms dislocate the $c$ axis (Fig. 2c, projecting along $b$ axis), and it be confirmed by the peak splitting in the pattern for $DyCu_2$. Cu and Ga atoms are random occupation and still hexagonal around Dy atom, whereas Dy atoms are located on both sides of $b$ axis alternatively rather than in the center of the hexagon, making the structure turns into orthogonal. Probably this staggered arrangement of rare earth atoms is the origin of giant magnetostriction of $RCu_2$ compounds because the R atoms are much easier to move along the $c$ axis.

The refined lattice parameters $a$, $b$, $c$, $a/c$ and volume $V$ are shown in Table 1. It is found that when small amounts of Cu substitute Ga in $DyGa_2$, the lattice obviously contracts along the $c$ axis, but expands in the $ab$ plane, resulting in the increase of $a/c$ ratio. The reason is that with the increase of $x$, the average Cu/Ga atomic radius decreases, and this leads to the lattice parameter $c$ which mainly depends on the distance of the R and Cu/Ga layers decreases. However, in order to compensate the Dy–Dy distance along the $c$ axis caused by $c$ decreasing, the lattice increases slightly in the $ab$ plane and the structure becomes more and more unstable with the increase in $x$. When $x$ reaches 0.6, the lattice parameters almost do not change, indicating that the Cu/Ga average atomic radius decrease to such a degree that the larger Dy atoms along the $c$ axis contact with each other and the structure becomes very unstable.

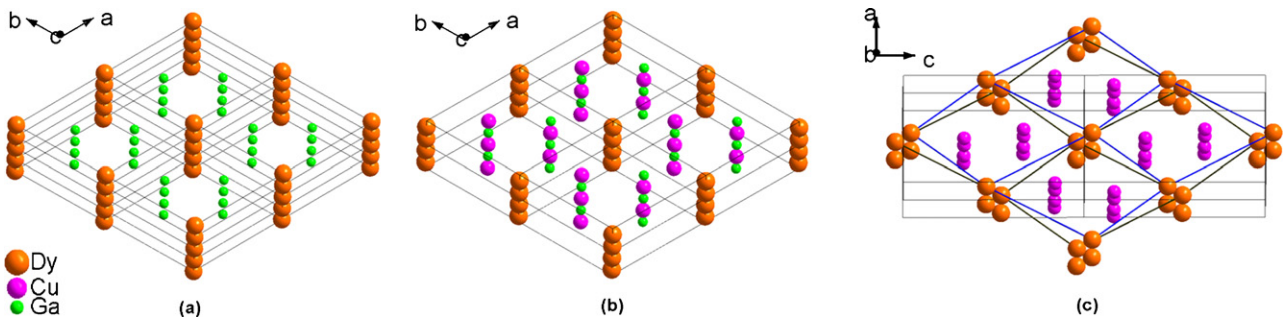


**Fig. 2.** The comparison diagram of the three crystal structures (a, b and c are corresponding to $AlB_2$-type, DyCuGe-type and $CeCu_2$-type structures, respectively).

**Table 1**
The lattice parameters of $DyCu_xGa_{2-x}$ (the values of $c$ and $V$ when $x = 0$, 0.2 is twice of the actual values for the convenience to comparison).

| $x$ | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $a/c$ | $x$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $a/c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 4.201 | 8.130 | 124.226 | 0.5167 | 0.7 | 4.369 | 7.069 | 7.470 | 230.690 | 0.5849 |
| 0.2 | 4.333 | 7.351 | 119.536 | 0.5894 | 0.8 | 4.367 | 7.040 | 7.453 | 229.159 | 0.5859 |
| | | | | | 1.0 | 4.359 | 6.996 | 7.438 | 226.825 | 0.5860 |
| 0.3 | 4.357 | 7.209 | 118.257 | 0.6044 | 1.2 | 4.349 | 6.970 | 7.400 | 224.303 | 0.5877 |
| 0.4 | 4.368 | 7.141 | 117.968 | 0.6117 | 1.4 | 4.342 | 6.934 | 7.363 | 221.667 | 0.5897 |
| 0.6 | 4.356 | 7.143 | 117.346 | 0.6098 | 1.6 | 4.333 | 6.887 | 7.332 | 218.789 | 0.5910 |
| | | | | | 1.8 | 4.319 | 6.841 | 7.309 | 215.944 | 0.5909 |
| | | | | | 2.0 | 4.299 | 6.794 | 7.290 | 212.907 | 0.5897 |

When $x$ further increases, Dy atoms no longer arrange linearly, but become staggered and form a $CeCu_2$-type orthogonal structure. In other words, the average atomic radius ratio of R to Cu/Ga is the key determinant for a compound to form $AlB_2$-type or $CeCu_2$-type structure.

For the compounds with $x > 0.7$, as Cu increases and Ga decreases, the lattice parameters $a$, $b$, $c$ and lattice cell volume decrease gradually.

### 3.2. Magnetic properties

The $M$ vs. $T$ and $1/\chi$ vs. $T$ curves of $DyCu_2$ are presented in Fig. 3. Through data fitting, $K$ (the slope of $1/\chi$–$T$ curve) is got to be 1.58 g/cm$^3$ T. By taking the molecular mass 289.59 g/mol into the equation $P_{eff} = (0.6359m/K)^{1/2}$ [16], the effective magnetic moment per molecular $P_{eff}$ is calculated to be 10.08 $\mu_B$. Meanwhile, the temperature of paramagnetic to antiferromagnetic phase transition is got to be 32 K as shown in the upper-right corner of Fig. 3, which is in good agreement with the value reported in the previous works [10].

Using the above methods, the effective magnetic moment and the Neel temperature $T_N$ of the $DyCu_xGa_{2-x}$ series are obtained and shown in Table 2. Because the abnormal knee of $x = 0.2$–0.6 around 113 K (will be discussed below) makes it difficult to obtain the $K$ value by linear fitting, the effective magnetic moments of these samples are not shown. The effective magnetic moments of the series ranging from 10.2 to 11.2 $\mu_B$, are consistent with the theoretical effective magnetic moment 10.63 $\mu_B$ of Dy ions. This indicates that the main contributor to the magnetization is 4f local electrons of Dy atom.

The temperature dependence of the magnetization of $DyCu_xGa_{2-x}$ ($x = 0$–2.0) have been measured from 3 to 150 K under an applied field of 50 Oe, and the typical curves are plotted in Fig. 4. The magnetization curves, except for that of $x = 0.2$, 0.4 and 0.6, are similar with the former works [10,14], which found $DyCu_2$

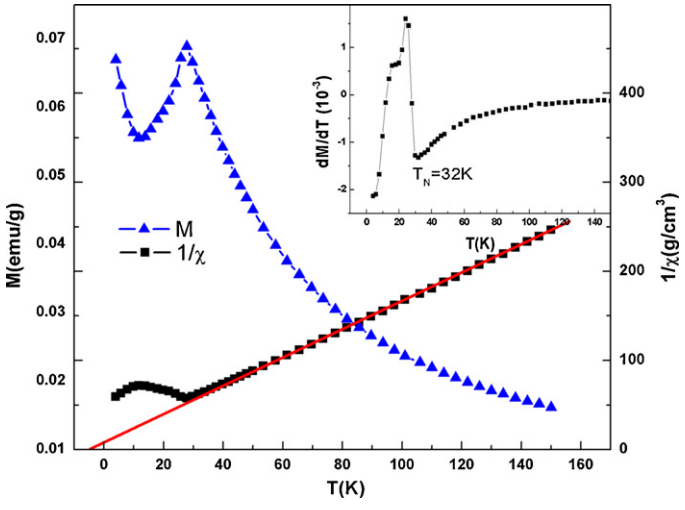


**Fig. 3.** The $M$–$T$ curve, $1/\chi$–$T$ curve and its linear fitting curve of $DyCu_2$ (for $H = 50$ Oe). The inset shows the differential curve of the magnetization curve.

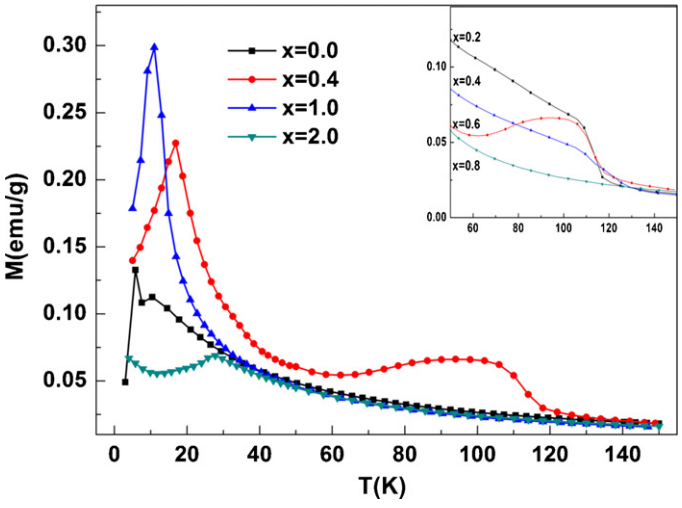


**Fig. 4.** Temperature dependence of the magnetization for $DyCu_xGa_{2-x}$ ($x = 0$, 0.4, 1.0, 2.0), $H = 50$ Oe. The inset shows the comparison of $DyCu_xGa_{2-x}$ ($x = 0.2$, 0.4, 0.6, 0.8) around 113 K.

**Table 2**
The effective magnetic moment and the Neel temperature of $DyCu_xGa_{2-x}$ ($H$ = 50 Oe).

| $DyCu_xGa_{2-x}$ | $x$ = 2.0 | $x$ = 1.8 | $x$ = 1.6 | $x$ = 1.4 | $x$ = 1.2 | $x$ = 1.0 | $x$ = 0.8 | $x$ = 0.7 | $x$ = 0.6 | $x$ = 0.4 | $x$ = 0.2 | $x$ = 0.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P_{eff}$ ($\mu_B$) | 10.8 | 10.7 | 10.3 | 10.2 | 10.3 | 10.5 | 10.8 | 10.2 | – | – | – | 11.2 |
| $T_N/T'_N$ (K) | 32.0 | 13.1 | 15.1 | 12.5 | 14.1 | 13.1 | 19.8 | 18.8 | 9.8/113.6 | 16.9/112.7 | –/113.0 | 6.6 |

and $DyGa_2$ are antiferromagnetic compounds. This suggests that most of these compounds show clear antiferromagnetic order at low temperatures. However, these curves have slightly difference, and it is demonstrated that the antiferromagnetic interaction of the compounds at low temperatures is different from each other, which is strongly related with the crystal structure. Besides, unlike those of $DyGa_2$ and $DyCu_xGa_{2-x}$ ($x$ = 0.7–2.0), the magnetization curves of $x$ = 0.2, 0.4 and 0.6 raise abnormally near 113 K, and the abnormal knee gradually decreases with the increase in $x$ (see insets of Fig. 4), which means the appearance of some kind of magnetic order in these compounds. Meanwhile, the isothermal magnetization curves of these compounds adjacent to 113 K are linear up to magnetic field of 5 T. This suggests that a paramagnetic to antiferromagnetic transition takes place in these three samples at about 113 K which is usually called high Neel temperature ($T'_N$). When temperature is cooled down to about 20 K, an antiferromagnetic to antiferromagnetic transition occurred. It is considered that the main reason to form the knee is the structure change caused by the ordered substitution of Ga by Cu. Owing to the substitution of Ga by Cu, the lattice parameter $c$ gradually contracts but expands in the $ab$ plane, which result in the change of the first and second nearest R–R distances. In addition, $M(T)$ for $DyGa_2$ shows a broad peak above $T_N$ centered on about 11 K. It is same with what reported in the previous work [14], and the substitution of Ga by Cu shifts the center of the broad peak of the $DyCu_xGa_{2-x}$ ($x$ = 0.2–0.6) to about 100 K. The main reason is considered to be the change of the near Dy–Dy distances which decrease with the increase in $x$ and the ordered substitution of Ga by Cu. However, as $x$ increases the crystal structure of $DyCu_xGa_{2-x}$ ($x$ = 0.7–2.0) completely changes, so those phenomenon disappears.

## 4. Conclusions

In conclusion, the $DyCu_xGa_{1-x}$ series crystallize in three phases, $AlB_2$-type ($x$ = 0–0.2), DyCuGe-type ($x$ = 0.3–0.6) and $CeCu_2$-type ($x$ = 0.7–2.0). The structure of $DyCu_xGa_{1-x}$ ($x$ = 0.3–0.6) is similar to the $x$ = 0–0.2, and the only difference is that the substitution of Ga by Cu is preferential; As $x$ continually increases, the lattice gradually contracts, and Dy atoms dislocate the $c$ axis, so the symmetry of the compounds reduces. Consequently, the average atomic radii ratio of R to Cu/Ga value controls the formation of structures. The magnetic-ordering transition of the compounds with $x$ = 0.2–0.6 takes place at two temperatures, about 113 K and 20 K, while those of other compounds only occurs at about 20 K, which is attributed to the change of the near Dy–Dy distances and the ordered substitution of Ga by Cu.

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