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Research Article

Keywords: High-entropy alloys, Rare earth, Ab initio simulation, Magnetization, Magnetocaloric effect

Posted Date: February 23rd, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1380255/v1>

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Magnetocaloric effect in ScGdHo medium-entropy alloy

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Received: date / Accepted: date

Abstract The search for effective solid-state refrigerant for magnetocaloric application is one of the mainstream topics in materials science. Rare-earth multi-principal element alloys seem to be promising candidates for these purposes. In this study, we address the issues of structure formation, magnetic and magnetocaloric properties in ScGdHo medium entropy alloy. We perform the *ab initio* molecular dynamics simulations for the liquid and solid phases in this system and reveal a strong tendency to form a single-phase solid solution. The experimentally fabricated alloy demonstrates a single-phase HCP crystalline structure with high density of defects. The magnetic measurements reveal a complicated magnetic behaviour in the material. The alloy exhibits antiferromagnetic or ferromagnetic behavior depending on the magnetic field. We have found that AFM order is preferable under a weak magnetic field and FM order occurs when the field strength exceeds 12 kOe. The alloy reveals a rather large coercive force in a wide temperature range up to the Neel point. The values of the magnetic entropy change and relative cooling power calculated for a magnetic field change of 0-5 T are $8.93 \text{ J/kg}^{-1}\text{K}^{-1}$ and 938 J/kg , respectively. The examined ScGdHo alloy demonstrates

the best magnetocaloric properties among similar rare-earth metal materials discovered to date.

Keywords High-entropy alloys · Rare earth · *Ab initio* simulation · Magnetization · Magnetocaloric effect

1 Introduction

Progress in the development of magnetocaloric refrigeration stimulates the search for novel high-performance solid-state refrigerants. Rare-earth based alloys and compounds seem to be promising materials for achieving these purposes due to the unique combination of huge magnetic moments and relatively high magnetic transition temperatures. By modifying the chemical composition and synthesis conditions, the magnetic and magnetocaloric properties in these materials can be tuned in a wide range. Note that among the rare-earth alloys explored so far, most of the studies are focused on the consideration of systems based on one principal element. Of particular interest are systems enriched in gadolinium. Gadolinium metal and its alloys in crystalline and amorphous states are often positioned as the best magnetocaloric refrigerants for different temperature ranges. Nevertheless, some metallic system based on other heavy rare-earth metals (Tb, Dy, Ho or Er) can demonstrate more favorable magnetocaloric properties compared with Gd-rich counterparts. So peak values of the magnetic entropy change in Gd-based glasses usually do not exceed $10.1 - 10.3 \text{ J/kg}^{-1}\text{K}^{-1}$ [1,2] for a field change of 5 T, while this parameter for Ho-, Er-, Tm-rich systems can achieve $10.76 \text{ J/kg}^{-1}\text{K}^{-1}$, $16.5 \text{ J/kg}^{-1}\text{K}^{-1}$ and $18.3 \text{ J/kg}^{-1}\text{K}^{-1}$, respectively [3–5]. Mixing several rare-earth metals into an alloy composition can also enhance a magnetocaloric response, as

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observed in glassy [6–8] and crystalline alloys [9, 10]. It is worth noting that in the case of binary Gd-Tb solid solutions [9], the largest caloric effect has been revealed in the alloy containing 30 % Tb. It means that a sufficiently high degree of substitution is needed to achieve the desired magnetic properties. In this context, rare-earth concentrated multi-principal-element systems or so-called high-entropy alloys (HEA) open up great perspectives in the search for efficient magnetic refrigerants. Recent studies of rare-earth HEAs have revealed complex magnetism and interesting caloric effects in these materials [11–19]. All these multicomponent alloys demonstrate strong magnetocaloric effect (MCE) over a wide temperature span (a table-like behavior) and consequently increased relative cooling power (RCP). Another interesting point is that some HEAs containing various rare-earth elements in their chemical composition can form dual-phase solid solutions including phases with rhombohedral and trigonal crystal symmetries, which is unusual for elemental rare-earth metals [12, 14]. Despite the fact that the single-phase formation in such systems can be complicated, these alloys demonstrate improved physical properties, especially when alloyed with scandium [20]. Note that both rare-earth binary and high-entropy systems are under extensive exploration, while medium-entropy alloys are still left out of consideration. Summarizing the issues mentioned, it seems reasonable to comprehensively analyze structure and magnetism in a rare-earth medium-entropy (MEA) system containing scandium. Thus, the aim of this study is to fabricate and explore the issues of phase formation, structure, magnetic properties and MCE on the example of ternary ScGdHo alloy.

2 Experiment and methods

The ternary ScGdHo alloy under consideration containing the rare-earth elements in an equal ratio was synthesized by melting of raw components in an arc-melter under a flowing helium atmosphere. The purity of the initial metals was about 99.9 wt. %. To ensure chemical homogeneity, the alloy ingot was inverted and re-melted at least five times. The actual chemical compositions of the fabricated alloy were checked by ICP-AES method (a Perkin Elmer Optima 8000 inductively coupled plasma atomic emission spectrometer). Crystalline structure of the material was checked with X-ray diffraction analysis using a Shimadzu XRD-7000 diffractometer with CuK α radiation, Ni filter, and graphite monochromator in a range of angles of 10–80° with a step $\Delta(2\theta) = 0.02^\circ$ and 3 s exposure at each step. Le-Bail refinement of the experimental XRD pattern was performed with FullProf Suite software [21].

Magnetic measurements were performed using a Cryogenic CFS-9T-CVTI vibrating sample magnetometer in the temperature range from 4 to 300 K and magnetic fields up to 50 kOe.

3 Results and discussion

3.1 *Ab initio* simulation

As we pointed out in the introduction section, the formation of a single-phase state in a concentrated rare-earth alloy is not an obvious fact. Note also that the alloy under consideration contains metals with drastically different atomic radii and therefore the segregation of elements and the formation of several phases is quite possible. Before fabricating the MEA containing scandium and performing its experimental study, it would be useful to somehow estimate the tendency of the alloy to form a single-phase solid solution. For these purposes, we analyze the liquid and solid phases in the system by the *ab initio* molecular dynamics simulations (AIMD). The AIMD calculations were performed within the framework of the density functional theory as implemented in VASP package [22]. Projector augmented-wave (PAW) pseudopotentials and PBE [23, 24] gradient approximation to the exchange-correlation functional was used [25].

When simulating the liquid phase, we consider a cubic supercell of 216 atoms (72 atoms of each type) at a temperature of 1713 K. The temperature was taken as an additive value of the melting points of pure components. The first property we extract from the calculations is the alloy density at 1713 K. To do that, we analyze the supercell volume as a function of mean total pressure in the system. The equilibrium density estimated in this way is 6375 kg/m³. This result can be compared with the density calculated via an additive approach:

$$\rho^{-1} = \sum_{i=1}^{N_c} x_i \rho_i^{-1}, \quad (1)$$

where x_i is mass fraction of i^{th} component. Using this ratio and experimental data for pure Gd [26], Ho [27] and Sc [28], we calculate the additive density of the alloy. The deviation between the ideal-mixture density and that obtained from the AIMD calculations does not exceed 0.73 %. It means that there are no specific strong interactions between the alloy elements.

Another important structural characteristic of the liquid phase to be considered is partial radial distribution functions (PRDFs) for the constituent elements. The RDFs for ScGdHo melt at 1713 K are shown in

Fig.1. We see that the radial functions for all pairs are similar; no specific pre-peaks or other structural features indicating local atomic order in the melt. This fact suggests weak chemical interaction between elements and a uniform mutual distribution of the alloy components in the space. In order to quantitatively characterize the local order in the melt, we calculate Warren-Cowley chemical short-range order parameters [29] from both total and partial coordination numbers as:

$$\alpha_{ij} = 1 - \frac{Z_{ij}}{c_j Z_{i-\text{all}}}, \quad (2)$$

here c_j is the j atom fraction; $Z_{i-\text{all}}$ and Z_{ij} are respectively the total and partial coordination numbers, which can be calculated from corresponding RDFs:

$$Z_{ij} = \frac{N_j}{V} \int_0^{r_{ij}^{\min}} 4\pi r^2 g(r)_{ij} dr, \quad (3)$$

where N_j - amount of j atoms in a system, and $r_{ij}^{\min}$ - position for the first minimum on PRDF. In the case of a random atom distribution, α_{ij} are equal to zero. As follows from our practice of studying Warren-Cowley parameters for multielement alloys [30,31], the values $|\alpha| < 0.05$ can be treated as zeros within the calculation accuracy. As seen in Fig.1, α_{ij} for all element pairs are around zero values. Based on these calculations, we conclude that the chemical interaction between alloy components is not intense. Thus, this system has a strong tendency to form a disordered single-phase solid solution.

In this study, we consider structure and properties of the alloy in crystalline state. And it would be useful to analyze the local order in the solid phase in this system with AIMD before experiments. Since all alloy components crystallize into a hexagonal close-packed structure (HCP), we expect the crystalline structure in the MEA to be the same. To analyze the structure of the solid phase, we simulated special quasirandom structure (SQS) with 162 atoms and performed calculations for 6 different random configurations to account for the effects of compositional disorder. Each SQS was relaxed at $2 \times 2 \times 2$ k-point mesh and then AIMD calculations in the isothermal-isobaric (NpT) ensemble were performed at 300 K. PRDFs obtained for HCP phase at room temperature are shown in Fig.2. Interatomic distances calculated from the radial functions are collected in Tab1. We find that R-R distances for all the pairs completely correspond to that expected from an additive approach, i.e. $d_{AB} = (d_{AA} + d_{BB})/2$. This result allows us to conclude that chemical interaction between alloy components is rather a weak and therefore the ScGdHo MEA can be treated as an exemplar of an ideal single-phase solid solution with an HCP structure.

Fig. 1 PRDFs and Warren-Cowley parameters of ScGdHo melt calculated at 1713 K.

Fig. 2 PRDFs of ScGdHo HCP SQS calculated at 300 K.

Table 1 Interatomic distances extracted from PRDFs of ScGdHo HCP SQS calculated at 300 K.

pair	interatomic distance, Å
Gd-Gd	3.475 ± 0.050
Gd-Ho	3.475 ± 0.050
Gd-Sc	3.425 ± 0.050
Ho-Ho	3.475 ± 0.050
Ho-Sc	3.425 ± 0.050
Sc-Sc	3.375 ± 0.050

3.2 Structural analysis

X-ray diffraction spectrum for the prepared alloy is shown in Fig.3. According to the structure refinement performed with the Le-Bail method, the MEA is a HCP single-phase solid solution with $P6_3/mmc$ symmetry. The calculated unit cell parameters: $a = 3.5240(2)$ Å, c

Fig. 3 Le-Bail refined XRD pattern for ScGdHo alloy.

$= 5.5575(4) \text{ \AA}$, $c/a = 1.577$. The experimental diffraction pattern has been fitted with the following convergence factors: $R_p = 5.97 \%$ and $R_{wp} = 7.78 \%$. Note that the diffraction lines are noticeably broadened, indicating high density of structural defects and micro-strains that take place in the material. This situation is natural for a system of this type. These structural features are inherent for many multi-element solid solutions that include elements with drastically different radii in their chemical compositions. In the case of ScGdHo alloy, scandium atoms are much smaller in size compared to other rare-earth elements. We suggest that scandium mainly contributes to the increased structural defectiveness in the MEA under consideration.

3.3 Magnetic and magnetocaloric properties

To detect magnetic phase transitions in the MEA, we have measured FC magnetization in a magnetic field of 50 Oe, see Fig.4. As follows from the obtained results, the alloy demonstrates a complicated behavior of the magnetization over the measured temperature interval. In the paramagnetic state, we see a typical Curie-Weiss dependence. When the temperature reaches about 109 K, a sharp bend in the magnetization is clearly observed. This anomaly can be interpreted as a Neel point in the material. Antiferromagnetic ordering is inherent for many rare-earth solid solutions, and this case is not an exception. Below the Neel temperature, the magnetization monotonically decreases and then tends to saturation. In the range of 70 - 40 K, the magnetization is practically independent of T . And when the temperature drops below 25 K, we see a sharp growth in the magnetic response. Identical low-temperature anomalies are observed in similar rare-earth alloys in small

Fig. 4 Temperature dependencies of FC magnetization and reciprocal magnetic susceptibility for ScGdHo alloy. The comments to the plots are given in the text.

magnetic fields [12, 18]. Depending on alloy composition and magnetic field, speromagnetic, asperomagnetic, or spin-glass magnetic states can be formed in these systems. According to the magnetic phase diagram derived for Gd-Tb-Dy-Ho-Lu hexagonal high-entropy alloy [18], type of magnetic ordering is a complicated function of both temperature and magnetic field. In the magnetic fields of the order of 5 - 10 kOe, the HEA can demonstrate antiferromagnetic (AFM) and ferromagnetic (FM) magnetic states. At a field strength of more than 12 kOe, only one magnetic transition from paramagnetic to ferromagnetic state occurs in Gd-Tb-Dy-Ho-Lu HEA. Magnetic measurements of the MEA at different magnetic field reveal identical behavior for $M(T)$ dependencies in comparison with those taken on similar systems [11, 12, 14, 16–19]. The ScGdHo alloy demonstrates a paramagnetic to antiferromagnetic transition at around 109 K when the magnetic field is less than 12 kOe and reveals a paramagnetic to ferromagnetic phase transformation in a field above 12 kOe. Based on the results obtained, we conclude that the nature of magnetic transitions in this MEA and other multicomponent rare-earth alloys is apparently the same.

In the paramagnetic region, the reciprocal magnetic susceptibility of the MEA depend non-linearly on temperature. Such behavior is rather unusual for an alloy containing rare earth metals with large magnetic moments. A roughly linear dependence of $\chi^{-1}(T)$ is often observed in similar multicomponent rare-earth systems [11, 12, 14, 16–19]. The classical Curie-Weiss law is usually applied to fit the magnetic susceptibility in the paramagnetic phase. In the case of the alloy under consideration, this approach is not suitable. Obviously, additional contributions in the alloy susceptibility should be accounted for to adequately describe the experimen-

tal data. We use for this purpose a generalized version of the Curie-Weiss law ($\chi = \chi_0 + C/(T - \Theta)$), which includes a temperature-independent term χ_0 describing the paramagnetic response from free electron gas and Van Vleck paramagnetism. The result of the best fitting is illustrated in Fig.4. We see that the generalized Curie-Weiss law adequately describes the paramagnetic susceptibility of the alloy. We obtain the paramagnetic Curie temperature Θ equal to 103.1 K, which indicates prevailing ferromagnetic interactions in the MEA. Note that the material is antiferromagnetic at weak magnetic fields but ferromagnetic at strong fields. A competition between antiferromagnetic and ferromagnetic correlations is the main reason for the complex nature of magnetism in the MEA. Based on the fitting, the effective magnetic moment was found to be $8.67 \mu_B$. Note that this value is noticeably larger than the theoretical one ($7.65 \mu_B$). Such an increase in the magnetic moment is usually associated with the magnetic polarization effects [16,32].

To further analyze magnetic behavior of the alloy, we have measured the magnetic hysteresis loop at 4 K, see Fig.5. The $M(H)$ dependence reveals a complicated shape, indicating changes in magnetic state of the material with varying magnetic field. One can see a bend in the magnetization curve near a field of ± 1.2 T (marked by arrows in Fig.5). This feature can be interpreted as a spin-flop transition, which is typical in the systems of this class [11,17]. We suggest that this situation takes place in the alloy under consideration. When a magnetic field is larger than the critical magnitude, the MEA demonstrates AFM - FM metamagnetic transition. This spin-flop transition is observed at all temperatures below the Neel point of the alloy. Another interesting feature we extract from the magnetization isotherms is large coercive force H_c . At $T = 4$ K, H_c has a peak value of about 12 kOe. Note that H_c decreases rapidly with increasing temperature. In the range of 30 - 70 K, the H_c values reduce from 3 kOe to 0.3 kOe. The observed coercive force values are too high in the context of the magnetocaloric applications of the alloy. This negative factor should be taken into account when considering the material as a magnetic refrigerant.

To estimate the magnetocaloric response in the MEA, we have calculated the magnetic entropy change ΔS_M and relative cooling power RCP (a measure of the quantity of heat transferred by magnetocaloric material during one cooling cycle):

$$\Delta S_M(T, H) = \sum \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \quad (4)$$

Fig. 5 Isothermal magnetization curves of the ScGdHo alloy at different temperatures. The upper plot - the hysteresis loop at 4 K. The arrows indicate a field-induced transition. The bottom plot - a set of the $M(H)$ dependencies obtained for the temperature range of 20 - 200 K. The shadowed areas in the bottom plot illustrate the magnitude of coercive force.

where M_i and M_{i+1} are values of magnetization at temperatures T_i and T_{i+1} , respectively; ΔH is intensity of applied magnetic field.

$$RCP = |\Delta S_M^{max}| \times \delta T_{FWHM} \quad (5)$$

where $|\Delta S_M^{max}|$ is the maximum isothermal magnetic entropy change, δT_{FWHM} is the full width at half maximum of $S_M(T)$ curve.

The magnetic entropy change dependencies calculated for different magnetic field are shown in Fig.6. We see that the $S_M(T)$ curves obtained for weak and strong magnetic fields are dissimilar. Obviously, this specific behavior is related to the spin-flop magnetic transition considered above. When the magnetic field is less than 12 kOe, the alloy demonstrates AFM order below the Neel point. The $S_M(T)$ calculated at 1 T (10 kOe) reveals a sign reversal in the magnetic entropy changes in the magnetically ordered state, see Fig.6. The $S_M(T)$ curves extracted for the fields of 2 - 5 T, where the material demonstrates FM state, are similar

Table 2 Magnetic and magnetocaloric characteristics of the rare-earth multicomponent alloys: the Neel point T_N , the peak value of the magnetic entropy change $|\Delta S_M^{max}|$ under a magnetic field change of 0-5 T, relative cooling power RCP under an applied magnetic field of 5 T.

alloy	T_N (K)	$ \Delta S_M^{max} $ ($\text{Jkg}^{-1}\text{K}^{-1}$)	RCP (Jkg^{-1})	Ref
GdTbDyHoEr	186	8.6	627	[14]
GdTbHoErY	163	5.4	453	[16]
GdTbHoEr	193	8.64	924	[19]
GdTbHoErLa	127	5.92	390	[19]
GdTbHoErLaY	120	5.85	245	[19]
GdTbHoErPr	135	6.92	498	[19]
GdHoSc	109	8.93	938	this study

Fig. 6 Temperature dependencies of the magnetic entropy changes in ScGdHo alloy under different magnetic fields. The dotted line shows the position of zero along the Y-axis.

each other. Note that all the high-field $S_M(T)$ functions reveals very broad peaks around the Neel point. Such a table-like behavior for the magnetocaloric effect has been recently found in rare-earth high-entropy alloys containing elements with drastically various radii, GdTbHoErLa and GdTbHoErLaY [19]. We can suggest that strong structural defectiveness caused by differences in atom radii is apparently one of the significant factors initiating the table-like behavior for MCE. In the case of the ScGdHo system, scandium has a much smaller atomic size compared to holmium and gadolinium. The experiment reveals that this alloy forms a highly defective crystal structure and demonstrates a table-like MCE. Besides a wide temperature interval for MCE, the MEA demonstrates high absolute values of the magnetic entropy changes. So the peak values of $|\Delta S_M^{max}|$ reach $8.93 \text{ Jkg}^{-1}\text{K}^{-1}$ under a magnetic field change of 0-5 T. This value is the largest magnetocaloric response observed among the concentrated rare-earth alloy discovered so far.

Another important MCE property of a refrigerant is its relative cooling power. We have estimated RCP in the MEA in the field range of 0 - 5 T as 938 J/kg .

All the magnetic and magnetocaloric characteristics obtained for the MEA in comparison with those revealed for similar rare-earth alloys are collected in Tab.2. As seen in the table, the GdHoSc alloy demonstrates the best magnetocaloric properties among analogous materials known to date. It can be concluded that this alloy is a very promising magnetic refrigerant for a certain temperature range. However, there are at least two negative aspects that need to be addressed before considering this material for technical applications. The serious problems are very high cost of scandium metal and large coercive force in the MEA. However, the study results reveal an interesting correlation between structural defectiveness and improved magnetocaloric response in rare-earth concentrated alloys. Thus, we conclude that enhanced MCE response in these rare-earth systems can be achieved by distorting the crystalline structure through micro-alloying, thermal annealing, or mechanical processing.

4 Conclusions

In this study, we analyze structure formation, magnetic and magnetocaloric properties in ScGdHo medium entropy alloy. The results of the *ab initio* molecular dynamics simulations performed for the liquid and solid phases reveal a weak chemical interaction between the alloy components and a strong tendency to form a single-phase solid solution. The alloy fabricated via standard arc-melting process demonstrates a single-phase HCP crystalline structure with high density of defects. The magnetic measurements reveal a complicated magnetic structure in the material. The Neel point in the studied MEA is about 109 K. Depending on magnetic field, the alloy exhibits antiferromagnetic or ferromagnetic behavior. We have found that AFM order is preferable under a weak magnetic field and FM order occurs when the field strength exceeds 12 kOe. In magnetically ordered state, the alloy reveals rather large coercive force up to the Neel point. The magnetic en-

ropy change and relative cooling power calculated for a magnetic field change of 0–5 T are $8.93 \text{ J kg}^{-1} \text{ K}^{-1}$ and 938 J/kg , respectively. The study results allow us to conclude that the fabricated ScGdHo alloy demonstrates the best magnetocaloric properties among analogous rare-earth materials discovered to date. Another conclusion we draw from this study is a correlation between structural defensiveness and magnetocaloric response in rare-earth concentrated alloys.

Acknowledgements This work was supported by Russian Science Foundation (grant 21-43-00015). Experiments were performed using scientific instruments included in the Collective Equipment Center "Ural-M" of the IMET UB RAS.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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