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# Full Length Article

# The influence of chemical impurities on the properties of heavy rare-earth metals (Tb, Dy, Ho): Experimental and theoretical approaches

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## ABSTRACT

The rare-earth metals, as academician A.E. Fersman aptly put it, have been called 'the vitamins of industry'. Over the past 80 years since their practical study has begun, these metals have become not just 'vitamins' but true 'vital preparations' without which it is difficult to imagine any branch of modern production. The scientific community has published hundreds of papers since 1937 on the unique magnetic properties of rare-earth metals (REM), as well as methods of manufacturing samples. Until now, the influence of chemical purity on the properties of REM has received relatively little attention. This work aims to eliminate this shortcoming and identify the main mechanisms of the influence of impurities on the properties of REM, as well as to suggest ways of their detailed analysis and study.

# 1. Introduction

Prior to World War II, few REMs were available to researchers in the form of metals (as metallic material) [1–3] (these works laid the foundation for a systematic study of the magnetic properties of REM). Development of techniques for ion exchange and extraction from solutions, as well as techniques for metals extraction from ores [4] made it possible to obtain the amount of pure metal that was necessary to ensure the current level of REM science. At the same time, the problem of the influence of purity on the physical properties of metals was raised for the first time in those years [5–7], but, as a rule, consideration was limited to the effect of oxygen on the properties of gadolinium due to the presence of the oxide in the metal, thus the anomaly observed in the low-temperature region is related to the present oxide [8–11].

A later experimental study of the critical behavior of polycrystalline dysprosium (residual resistivity ratio, RRR = 14) [12,13] found a significant difference (~1 K) between the values of the Neel temperature determined by three different methods: measurement of the heat capacity, magnetic susceptibility and electrical resistance. At the same time it was suggested that such a discrepancy may be due to the influence of impurities which is unequal with respect to different properties, that is, the stronger a given property is related to the crystal lattice, its phonon spectrum, the more significantly this property will depend on the impurity content. The validity of the assumption about the selective influence of impurities is confirmed by studies on single crystals [14–18]. The influence of impurities on the nuclear properties of heavy REM (gadolinium,

terbium, holmium) was studied by nuclear magnetic resonance method (NMR) [19–22] and using the IBPAD method (in-beam time-differential perturbed angular distribution) [23–25]. In both latter cases, the magnitudes of the ultrafine magnetic fields and nuclear quadrupole interactions were determined without discussing the influence of impurities on the macroscopic magnetic-thermal properties of heavy REMs.

Methods, physical and chemical foundations and theory, for the purification of REMs were developed in 1980–1990 of the last century. In recent decade, some of these methods were realized in China. However the interest in the purity of rare earths seems to be non-existent at the moment. Very few labs can afford high-purity rare earths, so there is really not much experimental research on rare earth impurities because there is no demand for it. The Materials Preparation Center (Ames Laboratory) has purity information on all new materials they make, but they are polycrystals - the single crystals are old and finding information on them is difficult. To estimate the purity of the old samples one can assume, quite safely, that their purity is at least on par with the purity of new polycrystals or better, so this may be the best practical approach right now. There is also a simple measurement to measure RRR [26–28] to determine samples' purity but nobody is doing it anymore in case of REM [29], there is also nobody to talk to about it.

The presence of local structure transformations significantly depends on impurities and defects in the samples, the influence of which is mentioned in a large number of theoretical works [30–32] and which goes beyond the research presented in this work, but will be continued by the team of the authors. This circumstance requires, first of all, a thorough experimental study [33].

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The most recent work to date that examines the effect of impurities in heavy REMs is [33]. In this case, a rigorous theoretical explanation of the influence of chemical purity on the properties of REM is missing. Some examples of changes in the magnetization of gadolinium depending on oxygen content are given [34,35], as well as increasing 'magnetic sensitivity' to the external magnetic field by the example of changes in the heat capacity of erbium depending on sample purity [36]. At the same time, an important observation is made regarding the importance of considering impurities in atomic, not weight, percentages. The atomic mass of heavy REMs is usually much greater than the atomic mass of the main impurities, so the representation of chemical purity in units of weight percent inevitably overestimates its value. In recent years, a number of works have been devoted to the study of the effect of hydrogenation (hydrogen as an impurity) on the properties of heavy REM [37-39]. Thus, in the ideal case, it is important to consider the specific number of impurity atoms, which opens up the prospect of using modern methods of mathematical modeling and numerical calculations in solving this problem, which was done in the present work.

## 2. Calculational details

Terbium, dysprosium, and holmium were chosen to calculate the density of states (DOS) including impurity atoms' influence by the method described in [40], since specific samples of these metals were carefully studied in the works of the authors [41-46], and there is reliable information regarding the chemical purity of the samples used. A unit cell of 128 atoms was used: 1 impurity atom per 127 metal atoms, thus, the impurity amount reached 0.8 at. %. Such ratio of impurity and metallic atoms, as a rule, occurs in practice (maximum level of any impurity in the 'dirtiest' REM samples does not exceed 1%, in the 'purest' samples-no more than  $0.1 \div 0.2\%$ ), at the same time, calculations of supercell, consisting of about 1000 atoms of rare-earth elements and 1 impurity (to provide the ratio of impurity in tenths of percent) require operative memory of about 1000 GB and essential massively parallel calculations, which take huge amount of machine time (about two years). In addition, the impurities can be located at interstices (interstitial impurities) and atomic positions (substitutional impurities). This, in general, depends on the size of the impurity atom. To accurately determine the position of the impurity atom, it is necessary to consider the phase diagram of the REM-impurity state. Formation of wide areas of solid solutions (except REM-REM) is extremely rare. Solubility of most metals (when formation of solid solution without structure change is possible) in REM is less than 0.1%. The impurity then leaves the solid solution as a compound with a different structure (eutectic or compound), which affects the magnetic properties and heat capacity. This paper uses the model according to which the impurity atoms are located only in the lattice sites, and the crystal structure does not change (remains hcp). For this reason, the calculations carried out in this work should be considered as model calculations that show the main trends in the electronic properties of REM in the presence of a particular impurity in the metal. Main trends in variations of magnetic-phase transition temperatures of metals differing in the purity can be indicated more clearly and in relation to the presence of 'magnetic' impurities (REM, Fe) and nonmagnetic impurities. In this case, it is of importance to consider the content of individual elements rather than the total purity. Thus we have chosen the most common magnetic and 'nonmagnetic' impurity elements in each metal for calculations: gas impurity (paramagnetic oxygen), 3d element impurity (ferromagnetic iron) and rare-earth impurity.

The DOS calculation was carried out in four steps. First, the crystal lattice parameters *a* and *c* and atoms' locations were determined. Then self-consistent charge density was calculated with a small number of points in *k*-lattice, then non-self-consistent calculations were performed using already fixed self-consistent charge density followed by DOS calculation. To achieve acceptable accuracy, it was sufficient to use an  $8 \times 8 \times 8$  *k*-lattice for self-consistent calculations and a  $10 \times 10 \times 12$  one for non-self-consistent ones. The pseudopotentials and kinetic energy cutoff

#### Table 1

Calculated parameters of electronic configurations of terbium, dysprosium, and holmium: pure metals and metals with impurity atoms.

Metal	$\mathbf{n}^{\uparrow}$	$\mathbf{n}^{\downarrow}$	$E_{\rm f}$ , eV	Р	g(E <sub>f</sub> ), E
ть	190.6	190.9	3.18	0.001	438
Tb + O	189.6	195.3	3.14	0.015	225
Tb + Fe	189	197.1	3.16	0.021	328
Tb + Gd	192.1	189.9	3.18	0.006	437
Но	199.9	181.1	2.91	0.049	337
Ho + O	186.5	200.3	2.91	0.036	210
Ho + Fe	182.4	207.2	2.9	0.064	227
Ho + Dy	179.9	198.6	2.91	0.049	383.5
Dy	205.5	180.7	3.04	0.064	336.5
Dy + O	199.3	184.3	3.04	0.039	254.9
Dy + Fe	182.1	206	3.07	0.061	223.3
Dy + Er	179.2	207.7	3.04	0.074	345.6

parameters for the wave functions and for the charge density were selected from the library of standard solid-state pseudopotentials (SSSP) [47,48]. Since the SSSPs for REM are scalar, the calculations do not take into account the spin-orbit interaction. That is why the magnetic moments of Tb, Ho, Dy (5.9, 3.7, 4.7  $\mu_B$ ) calculated in the present paper are less than the previously published theoretical and experimental values [49,50]. At the same time, a similar calculation for Gd (spin-orbit interaction in Gd is absent) gives the value of the magnetic moment of the atom equal to 7.4  $\mu_B$ , which corresponds exactly to previously published theoretical and experimental values. Thus, the development of fully relativistic pseudopotentials for REM is an important theoretical task because of the significant influence of the spin-orbit interaction on the magnetic properties of REM.

# 3. Results and discussion

Analysis of the electronic properties of rare-earth materials with impurities is important to consider as a priority, since the electronic structure largely determines the macroscopic properties of conducting materials. All densities of electronic configurations of pure 4f elements are characterized by the presence of a 4f zone split into two narrow parts (Fig. 1). One of them is completely filled and lies well below the Fermi level, while the other is not filled. The strong electron-electron interaction between the 4f electrons leads to localization of magnetic moments and partial spin polarization. This result was known earlier and was described in [51].

Adding an impurity to the REM crystal lattice leads to an inevitable transformation of the type of electron state density and a shift of the Fermi level. Since the electrons in the *4f* zone are rather narrowly localized by energy, a small shift of the Fermi level leads to a sharp change in the DOS value. It is expected that such a significant change in the electronic structure causes a change in the physical macroscopic properties of the material, which are determined by the density of electronic states at the Fermi level.

Thus, in the present work for terbium, dysprosium, and holmium with impurity atoms, the Fermi energy, spin polarizations, and densities of electronic states at the Fermi level were determined (Table 1).

The calculated DOS values for terbium are shown in Fig. 1.

The general look of DOS plots when one metal atom is replaced by an impurity atom does not change significantly. Only the position of the Fermi energy level, and the corresponding density of electronic states on it, varies. This can explain the fact that the experimental resistance results for REM of different purity can differ significantly [12,18]. There is also a slight increase in spin polarization with the addition of impurity, as there is an increase in the *s*-*p*-*d* zones. However, this increase in polarization is small, since the contribution of electrons from the 4*f* zone is more significant. The addition of the impurity of another rare-earth



Fig. 1. Densities of states (DOS) of metallic Tb and terbium with impurity atoms of oxygen, iron, gadolinium. Negative DOS values correspond to spin 'down', positive values-to spin 'up' (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).



Fig. 2. Densities of states (DOS) of metallic Ho and holmium with impurity atoms of oxygen, iron and dysprosium. Negative DOS values correspond to spin 'down', positive values-to spin 'up' (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

element, gadolinium, has almost no effect on the electronic structure of the substance.

Calculated DOS values for holmium are presented in Fig. 2.

For holmium, as well as for terbium, there is a slight change in the Fermi energy level and the density of electronic states on it. The addition of iron impurity leads to an increase in spin polarization due to an increase in the d zone. An atom of another rare-earth element, dysprosium, is considered as an impurity atom. The electronic properties of the system with dysprosium differ slightly from the pure matter.

The calculated DOS values for dysprosium are presented in Fig. 3.

The spin polarization of the system increases slightly with the addition of an atom from the 3d group (in this case it is an iron atom). This may be due to hybridization of the *f*-*d* zone, which leads to reorientation of spins from the 3d zone. In other cases, the presence of impurity atoms

affects the type of electron density distribution in much the same way as in the cases already considered.

Addition of impurity also distorts the crystalline hexagonal lattice of REM, as evidenced by the change in the average calculated lattice parameters, *a* and *c* (Table 2). The term 'average' is used in the sense that in this paper a supercell consisting of 128 is considered as a unit cell; it is the minimum symmetry in our case. Therefore, the rare-earth metal in the present work is considered to consist of such supercells, respectively, the lattice parameters are calculated for the supercell. In this regard, it is correct to speak about the true lattice parameters of the hcp lattice only in the case of pure metal; in the case of adding impurity, the obtained calculated value of the supercell parameters is divided by four, resulting in an 'average' value of the hcp lattice parameters with impurity taken into account.



Fig. 3. Densities of states (DOS) of metallic Dy and dysprosium with impurity atoms of oxygen, iron and erbium. Negative DOS values correspond to spin 'down', positive values- to spin 'up' (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

Table 2			
Average lattice parame	ters, a and c, depending	on the type of imp	urity atom (Å)

	а	с		а	с		а	с
Dy	3.613	5.758	Но	3.591	5.691	Tb	3.577	5.868
$\mathbf{D}\mathbf{y} + \mathbf{O}$	3.590	5.763	Ho+O	3.596	5.644	Tb + O	3.650	5.626
Dy + Fe	3.576	5.754	Ho+Fe	3.568	5.715	Tb + Fe	3.582	5.843
Dy + Er	3.612	5.756	Ho+Dy	3.591	5.692	Tb + Gd	3.578	5.869

There is a good agreement between the lattice parameters of the hcp for pure metals and the experimental data, which are (for the parameter a) 3.601, 3.590  $\mu$  3.577 for Tb, Dy and Ho, respectively [49]. Some overestimation of the theoretical values is due to the failure to take into account the spin-orbit interaction in the model. Due to the inability to simulate an impurity atom in a particular place of the crystal lattice, it is difficult to establish an unambiguous direction of lattice distortion (compression/extension), and it is observed in all cases and does not exceed 1–2%. Schematically, one of the options for possible distortion of the crystal lattice is shown in Fig. 4.

Thus, calculations from first principles show that the addition of impurity shifts the Fermi energy level, which leads to a change in the density of electronic states at the Fermi energy level and, accordingly, changes the value of spin polarization. The decrease in DOS with the addition of oxygen or iron is consistent with the experimental fact that the resistivity of pure materials is less than that of materials with impurities. The contribution of the 3d group atom impurity, which increases the spin polarization of the system, is worth noting separately. The impurity of a rare-earth metal insignificantly affects the electronic structure of the sample, which is related to the failure to account for the spin-orbit interaction in the scalar pseudopotentials used for the calculations, and is an obvious limitation of the model used, except for the gadolinium impurity, in which the spin-orbit interaction is zero.

The purest heavy REMs samples to date are considered to have been produced in [52,53]: Er of the 99.97 at.% (99.996 wt%) purity and Gd-99.94 at.%.

It is also important to pay attention to different methods of manufacturing of heavy REM of different subgroups, which also influence the predominant presence of certain impurities in the considered metals. As a rule, REM samples are cut from a single crystal grown by the method called 'Ames method' [4], according to which the preparation of highpurity REM begins with the preparation of pure oxide. Since most of the cationic impurities that are present in the oxide will inevitably get into the final metal sample, it is critical to ensure maximum purity of the initial oxide. Exceptions are volatile impurities that evaporate during the subsequent vacuum melting of REM, such as alkali and alkaline earth metals. Then a procedure of metallothermic reduction of REM fluoride compounds is carried out. This stage is subdivided into three varieties depending on REM being prepared. In case of producing Gd or Tb single crystals the method is used for so the called second group of REM, namely Y, Gd, Tb, Lu, i.e. for metals with relatively low melting points, but high boiling points. Accordingly, Gd may occur more often as an impurity in Tb and vice versa. In turn, Dy and Ho belong to the so-called third group of rare earth metals, which also includes Sc, Er and Tm. The melting temperatures of the third group metals are approximately in the same range as the corresponding temperatures for the second group metals, but their vapor pressure values are much higher. Thus, purification of these metals by evaporation is much easier. Introduced impurities such as N, C, O, which form stable compounds, remain when the metals are sublimated at low sublimation rates (e.g., for Ho 2.1 g/h). Therefore, for the third group of metals, and Ho in particular, no so much attention is paid to removing oxygen from the fluoride and preventing its introduction into the metal, since oxygen and other impurities, as well as the tantalum impurity, are removed from the metal during the sublimation step. In this regard, other REMs that may occur in Dy and Ho as impurities are also somewhat different from the case of Tb and Gd. Recently, the preparation of pure REMs, which begins from the preparation of pure oxides, was realized in China [54,55].

In addition to theoretical calculations, this paper makes the first attempt to systematically describe the influence of chemical impurities on the macroscopic magnetic-thermal properties of heavy REM, namely, high-purity Tb, Dy and Ho, information on the chemical purity of which



**Fig. 4.** The distortion of the hcp crystal lattice of Ho with the adding of Fe impurity atom (based on the calculation results) (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

is known reliably [41–43]. Field dependences of magnetization for samples of different purity are presented in Fig. 5.

The general trend is an increase in the saturation magnetization of 'dirty' samples at the same temperature over the corresponding values of 'clean' samples in the region of ferromagnetic and, partially, antiferromagnetic ordering. The shift of FM-AFM phase transition towards lower temperatures is also observed, and it is sharper for 'dirty' samples. This circumstance is probably related to the presence of significant amounts of impurities with magnetic ordering in the 'dirty' samples (other heavy REM impurities: Er, Y, Gd, Dy in terbium samples (up to 1000 ppm), Ho in dysprosium samples (up to 2000 ppm) [for comparison: in the up-todate high-purity single-crystalline samples the impurity level of all other lanthanides (relative to the reference metal) is 10-20 ppm]; iron up to 2000 ppm [for comparison: in up-to-date samples the impurity level of iron does not exceed 30 ppm]). The level of gas impurities, which make the main contribution to changes in the chemical composition of heavy REM, in 'pure' and 'dirty' samples is practically the same (for example, oxygen in terbium-1900 ppm for both samples; nitrogen-180 ppm in 'pure' [41] and 200 ppm-in the 'dirty' one [56]). The example of dysprosium (Fig. 5) demonstrates that the saturation field for samples with different impurity contents is different. This behavior can be explained by the dependence of the magnetocrystalline anisotropy constant on the lattice distortion due to the presence of an impurity. The addition of an impurity atom to the crystal lattice of a rare-earth metal leads to a local disorder of the lattice and the violation of its symmetry.

Additional analysis of the magnetization temperature dependencies of purity (Fig. 6) allows to propose a mechanism of magnetic impurities (REM) influence on magnetization.

The magnetic impurity in heavy REM, which role, as a rule, is played by other *4f* elements (their content is maximal relative to other impurity elements in 'dirty' samples) becomes the local impurity center of ferromagnetic ordering (similar to the center of crystallization or boiling). This assumption is physically justified, since the transition at the Curie temperature in REM is always the first order phase transition (FOPT). As the magnetic field and temperature increase, the phase state of all heavy REMs first undergoes FOPT (at the Curie temperature) and then SOPT (second order phase transition) (often mixed) (at Neel temperature) [40]. Accordingly, in each case there is a certain probability of the existence of a local nucleation center from which the phase transition begins. In this case, the magnetic moment of the impurity center may exceed the magnetic moment of the reference metal atom (for example, the magnetic moment of the Ho impurity in the dysprosium sample is greater than the atomic magnetic moment of Dy [57,59]). Accordingly, the magnetic moment of the impurity is more susceptible to the external magnetic field even in the case of relatively low fields, and therefore the FM ordering in the impurity center comes faster than in the main volume of the reference 'pure' metal, taking into account the small value of the impurity concentration ( $\sim 1-2$  impurity atoms/1000 reference atoms in real samples). There is an exchange interaction between magnetic moments of the impurity and the magnetic moments of the base metal. Additional (to the exchange between the magnetic moments of the 'pure' metal) interaction contributes to the faster establishment of the FM ordering throughout the sample in a given range of magnetic fields and temperatures, which is experimentally manifested in the higher values of magnetization in the region of low fields and lower temperatures of phase transitions in the 'dirty' samples compared to the 'clean'. The tendency of the transition shift towards lower temperatures persists in the AFM ordering region of the reference metal: the phase transitions in the 'dirty' samples occur at lower temperatures than in the 'clean' ones. The insets of Fig. 6 show the dependencies of the Neel temperature of both samples on the value of the external magnetic field: in both cases (Dy and Ho) the value of the Neel temperature of the 'dirty' sample is lower than that of the 'clean' one. An alternative mechanism that can explain this fact is that the impurity atom deforms the crystal lattice, due to which the lattice parameters of the adjacent layers are mismatched, thus the transition can be completely suppressed, or the phase transition temperature can decrease, which is observed in the experiment in bulk samples and REM thin films [60,61]. An additional feature in the region of the Neel temperature is that the magnetization of 'clean' samples practically coincides in magnitude with the magnetization of 'dirty' samples. The additional magnetic moment of the impurity atom/atoms has already undergone ordering in relatively low fields, and further increasing the field cannot change its magnitude and direction, so the contribution of the impurity magnetic moment remains constant and has almost no effect on the total magnetization in the higher field region. The impurity atoms are usually unevenly distributed over the sample volume, which is associated with the peculiarities of the REM single crystals fabrication method [62]. Inhomogeneous distribution of impurities in crystallites at metal evaporation and deposition on a copper water-cooled condenser is caused by the distillation process itself. At first metal degassing is carried out, at which easily volatile impurities (sodium, etc.) evaporate, thus the first portions of distillate and the edge



**Fig. 5.** Field dependences of magnetization of single-crystalline samples of terbium, dysprosium, and holmium. The data from this and previous works [41,42,44,45] is compared with literature data: Tb [56], Dy [43,57], Ho [58] (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).



Fig. 6. Temperature dependencies of magnetization of single-crystalline samples of dysprosium and holmium. The data from this and previous works [42–45] is compared with literature data: Dy [57], Ho [58] (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

of crystallites which is the closest to the copper condenser are contaminated by these metals. Further, the impurities evaporate according to their vapor pressure. Refractory metals and oxides R-O and R-O<sub>2</sub> remain in the residue. Thus, impurity clusters (places of the highest impurity concentration in the sample) of other REMs undergo a cascade of FM-APM-PM phase transitions themselves [40], so it is possible that by the time of the AFM-PM transition at the Neel temperature, the magnetic state of the impurity is an antiferromagnetic or paramagnetic, which does not contribute significantly to the total magnetization value. Given the monotonic decrease in the Curie and Neel temperatures in the series from gadolinium to thulium, this assumption is correct. For example, in the considered Dy 'dirty' sample the main REM impurities are holmium and erbium [57], whose phase transition temperatures are significantly lower than similar dysprosium temperatures [40]. Vice versa, an impu-



**Fig. 7.** Temperature dependences of the heat capacity of single-crystalline samples of terbium, dysprosium and holmium. The data from this and previous works [41,42,44–46] is compared with literature data: Tb-[63], Dy-[14,43,64], Ho-[65,66] (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

rity of dysprosium in a Ho 'dirty' sample [58], (0,04 wt%), influences the location of the Neel temperature in such a way that its values for 'clean' and 'dirty' samples practically coincide (Fig. 6): dysprosium cluster impurity undergoes an AFM-PM phase transition at 179 K, which is 48 K higher than the Neel temperature in holmium. In the case where the main impurity is gadolinium (ferromagnetically ordered up to room temperatures), its contribution to the magnetization of the main metal remains unchanged regardless of the magnetic field value according to the mechanism proposed above.

Thus, the main influence on the magnetic properties of heavy REMs is exerted by impurities of other elements whose influence is especially noticeable in relatively low fields, in the FM ordering region of the reference metal; it is leveled in the AFM region and disappears altogether in the PM region.

The proposed mechanism of impurity influence through the formation of a local impurity center as the point of phase transition initiation is also confirmed in the analysis of the heat capacity dependencies of terbium, dysprosium, and holmium on the samples' purity (Fig. 7). It is important to emphasize that studies of the heat capacity of REM singlecrystalline samples are extremely rare (in the present work we found all articles that deal with the heat capacity of terbium, dysprosium, and holmium and have at least some information about the chemical purity of the samples).

Thus, in all 'dirty' samples the FM-AFM transition occurs at lower temperatures than in 'clean' ones, the Neel temperatures of both types of samples practically coincide, except for polycrystalline samples, in which the FM-AFM transition also occurs at lower temperatures. This is due to the extremely poor degree of purification of polycrystalline samples made in the 1950s (no other information is available in literature). Double- distilled Dy [14] which RRR value was 210, but the sample was a druze (a state of fused crystals). In this regard, the question of its single-crystalline state is debatable. It is also important to note the almost complete suppression of the anomaly associated with the FM-AFM phase transition at the Curie temperature in 'dirty' samples. The spiral AFM structure is a long-period structure that occupies several planes of the crystal lattice. The impurity center as if 'locks' the helix propagation (prevents the spin rotation in the next layer), limiting the growth of the AFM structure. For the same reason other anomalies in the 'dirty' samples on the temperature dependences of the heat capacity, which appear in a non-zero magnetic field are absent. They are associated with the



**Fig. 8.** Temperature dependencies of the magnetic part of the heat capacity of single-crystalline samples of terbium, dysprosium, and holmium (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

emergence of spin-slip structures. The energy of such structures differs little from that of the helical AFM structure (in fact, they are distorted spirals): the impurity center also interferes with the 'natural' orientation of spins in a spin-slip type structure. Accordingly, the detection of intermediate metastable phases in 'dirty' samples is virtually impossible. This effect is leveled out in the region of the Neel temperature, where the value of the heat capacity peaks is approximately the same.

In addition to the total heat capacity, this paper considers the magnetic contributions to the heat capacity of terbium, dysprosium, and holmium (Fig. 8).

This part of the heat capacity is the most sensitive to changes in the chemical composition of the studied metals, especially in the presence of sufficient amounts of magnetic impurities. From the total heat capacity according to the data in [41-43] the magnetic contribution  $C_M(T, H)$  to the heat capacity was calculated according to the following procedure. In our model, the lattice and electron heat capacities do not depend on the magnetic field, and their values are assumed to be the same for all rare-earth metals, including the paramagnetic lanthanum and lutetium. Thus, the heat capacity values for La and Lu (there is no magnetic contribution to the heat capacity of these metals), were obtained experimentally. The sum of the electron and lattice heat capacities of Gd (for example) is calculated according to the proportional distribution of the experimental values of the heat capacities of La and Lu according to the relation  $C_L(Gd) + C_{el}(Gd) = 0.5C_p(La) + 0.5C_p(Lu)$ , where  $C_p$ -experimental values of heat capacity of nonmagnetic REM. The coefficients correspond to the fact that Gd is exactly in the middle of the REM series. For example, for Tb this empirical rule is modified to  $C_L(Tb) + C_{el}(Tb) = 6/14C_p(La) + 8/14(Lu)$  etc. The calculated contribution was then subtracted from the experimental values of the total heat capacity.

The magnetic heat capacity in this paper is analyzed within the framework of the theory of the emergence of the energy gap  $\Delta$  in the spectra of spin waves existing in ferromagnetic materials with a hcp crystal lattice and magnetic anisotropy between the vertical axis of hcp and the basal plane [67]. The energy gap is the minimum energy required to excite a spin wave (in the case of an REM, a helical AFM structure); its appearance is due to the need to perform work against

magnetic anisotropy forces (between the basal plane and the vertical axis) to rotate the spin when moving from one crystal plane to another within the formation of a long-period (usually helical) structure in REM, so  $\Delta \sim \sqrt{K_2 K_6}$ . Based on this theory, in [68,69] a general relationship for the magnetic part of the heat capacity in the low temperature region was obtained:  $C_M = AT^{3/2}exp(-\Delta/k_BT)$ . It was experimentally verified for all heavy REMs in a 1966 paper [70], The authors themselves point out that 'the best-fit expressions often turn out to be questionable, and more work is required before it can be confidently assumed that the observational results and interpretation of the magnetic contributions are made accurately'. Such work was later done only for single-crystalline terbium [71] by analyzing various experimental data on the magnetic heat capacity at low temperatures available at that time. It is important to note that the authors of [71] indicate that it is the presence of impurities that precludes accurate determination of the various contributions to the heat capacity, which entails incorrect determination of parameters, in particular, the value of the energy gap.

Thus, in the present work, all currently available data on the magnetic heat capacity of single-crystalline dysprosium at low temperatures were approximated by exponential dependence (Fig. 9), including those obtained on high-purity single crystal [43,45], and the contributions to the magnetic heat capacity of holmium and terbium were analyzed.

Approximation of the data allowed determining the values of the energy gap for dysprosium samples of different purity (Table 3).

There is an inverse dependence between the concentration of nonmagnetic impurity (oxygen) and the value of the energy gap in the spectrum of spin waves. In the considered temperature range (for which only the exponential approximation of the magnetic part of the heat capacity is valid), the dysprosium oxide has a significant effect on the magnetocrystalline anisotropy value. The anisotropy value is directly related to the value of the crystal field: the additional contribution from the oxide is  $\sim kT$  [70] and, obviously, it depends on the amount of formed oxide, which is in direct dependence on the oxygen impurity concentration. For the same reason, the data obtained allow to draw an indirect conclusion about the experimentally observed distortion of the crystal lattice when adding an impurity (due to changes in the crystal field parameters depending on the impurity content).



**Fig. 9.** Approximation of the magnetic heat capacity of dysprosium in the low temperature region. Experimental data are taken from [14,43,70](For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

Table 3
Type of the observed magnetic heat capacity temperature dependence of Dy for samples of different chemical purity.

Type of temperature dependence	Approximation interval, K	Purity, wt%	Energy gap in the spin wave spectrum, K	Oxygen content, wt.%	References
$C_{M} = 107T^{3/2}exp(-31/T)$ $C_{M} = 95T^{3/2}exp(-43/T)$	9 – 20 9 – 30	99.47 99.98	31 43	0.092 0.06	[70] [43,45]
$C_M = 80T^{3/2}exp(-49/T)$	7 – 30	99.996	49	0.01	[14]

Structural studies of the samples were not carried out in the present work, and the traditional technique of X-ray diffraction is not likely to detect the minor lattice distortions predicted theoretically (Table 2). Experimental detection of the stated changes in crystal lattice parameters requires the use of modern structural analysis methods, such as EXAFS, in conjunction with high resolution scanning microscopy (EBSD), which will be performed in our future studies.

Heat capacity anomalies of another type, also associated with the presence of the oxide and described earlier, were observed in gadolinium [7,70]: heat capacity initially decreases to  $\sim 4$  K, which is not observed in dysprosium. The appearance of anomalies was explained in [9]: it is associated with the presence of gadolinium oxide phases, which undergoes a phase transition in the region of ultra-low temperatures (about 3 K) and, thus, the reduction of the oxide heat capacity affects the reduction of the total heat capacity value in the region of ultra-low temperatures. This behavior is characteristic of gadolinium samples with significant oxygen content as an impurity (0.2 wt%) [70].

A similar behavior of heat capacity was previously observed in polycrystalline holmium [72,73] with oxygen content 0.21 wt.%. In this case, according to the entropy calculations performed in [73], holmium oxides have no effect on the behavior of the heat capacity at low temperatures. In the present study, a similar behavior of the heat capacity (the magnetic part of the heat capacity also decreases at temperatures below 4 K) was observed in a single-crystalline sample with insignificant oxygen content-0.02 at.% [42]. This behavior is in agreement with literature data at T < 4 K (Table 4).

In [72] the following empirical temperature dependence is introduced for the heat capacity of holmium in the low temperature region:  $C_p(mJ/mol \cdot K) = 2.26T^3 + 10T + C_N$ , where  $C_N$  is the nuclear heat capacity. Calculation of the nuclear heat capacity using data for a single crystal (Table 4) shows that in the region of temperatures below 2.5 K, the nuclear heat capacity is 95–99% of the total value of the heat capacity, and this contribution sharply decreases with increasing temperature (about 50% at 4 K). Thus, the decrease in heat capacity from the starting temperature ( $\sim$ 1.5–1.6 K) to  $\sim$ 5 K in holmium is probably due to the large value of the nuclear heat capacity at temperatures below 2.5 K. A similar situation is observed in single-crystalline terbium. The influence of impurities in this case (unlike dysprosium) is not observed for both 'dirty' and 'clean' samples.

The nuclear heat capacity is extremely sensitive to the presence of impurity atoms. For this reason (accounting for nuclear interactions) it is also reasonable to use the Mössbauer effect to study the influence of impurities [74,75]. These studies were conducted on a very limited set of REM and impurity centers, in fact, only tin always acted as an impurity. The resumption of such studies to achieve the goals of the work is very reasonable.

The results of the analysis of the effect of impurities on the magneticthermal properties of REM are summarized in the form of magnetic phase diagrams of metals constructed both from the data of this work and taken from the literature (Fig. 10).

It can be noted that the phase transition temperatures shift towards lower temperatures in 'dirty' samples (in the case of predominance of magnetic impurities), which facilitates the formation of magnetic ordering with a large value of moment (*e.g.*, FM) in the region of low fields. At the same time there is an increase in the value of critical fields of the phase transition (in the case of predominance of nonmagnetic impurities), which complicates or expands the region of phase transformation between antiferromagnetic (AFM) and metastable magnetic structures (fan, helifan). The impurity prevents the formation of the 'classical' AFM helix, distorting and even destroying it. Thus, the evolution of the phase transition in 'dirty' samples changes. The impurity in this case is a pinch point, and, accordingly, a larger value of the external magnetic field is necessary to change the initial state. In general, a greater diversity of





Fig. 10. Comparison of magnetic phase diagrams of single-crystalline Tb [41,76–79], Dy [43,80–82] and Ho [42,83,84] depending on the chemical purity of the samples (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

#### Table 4

Comparison of experimental data on the heat capacity of holmium obtained in this paper in the low-temperature region and data from the paper [72].

This paper		Data from [72] (Table III)			
T (K)	C (J/mol K)	T (K)	C (J/mol K)		
1.625	1.56309	1.481	1.5809		
2.058	0.97329	2.1117	0.915		
3.811	0.40637	3.8353	0.460		

spin structures is observed in the 'clean' samples compared to the 'dirty' ones.

#### Table 4

Depending on their chemical purity, allotropic modifications of REM are also observed [85,86], at the same time in [33] it is emphasized that new phases can form solely due to the influence of impurities, actually being a 'response' to the external magnetic field on the part of the impurity atom or their compounds, rather than the base material itself [87,88].

Another type of defects that affect the properties of heavy REMs is the appearance of dislocations associated with sample deformation. It is known that during its movement in a crystal lattice, a dislocation overcomes various kinds of energy barriers. The braking is carried out either by elementary excitations in the crystal volume (for example, phonons), or by the potential relief of the lattice itself - the Peierls–Nabarro stresses [89–92]. The presence of other lattice defects, such as vacancies, impurity and interstitial atoms, can lead to a similar effect. A rigorous assessment of the relative influence of the potential lattice relief and the force fields of point defects on dislocation mobility in various crystal structures is currently lacking. A detailed study requires compression/extension experiments on the same high-purity REM samples.

## 4. Conclusion

The presence of other chemical elements' impurities in heavy bulk single-crystalline samples of REM leads to lower temperatures and increased values of the critical fields of phase transitions, thereby complicating the restructuring of the magnetic structure. At the same time, this conclusion is unfair in the case of nanocrystalline rare-earth metals [93]. The influence of impurities explains the presence of local spin defects (spin slip type structures) and the variety of magnetic 'allotropic' modifications of heavy REM. Due to impurities, the density of states at the Fermi level becomes nonzero. The addition of impurities distorts the hcp crystal lattice with a change in its parameters by 1–2%. The present work considers the influence of impurities on the properties, including crystalline ones, of single-crystalline bulk samples, whereas the opposite influence of the crystal state - the perfection of the structure (absence of grain boundaries and structural defects, reduced dislocation density, etc.), measurements of macroscopic properties along the light and hard directions of the single crystal-on the behavior of impurity atoms is not considered. Moreover, the same applies to the nanostructured state, in which completely different effects related to the increasing role of the surface, nanoscale grains, etc. are observed, which should be the subject of a separate study, e.g. [94].

The analysis of the impurities influence on the properties of heavy REM undoubtedly requires clarification, although this paper lays down possible trajectories for future studies. In this case, for the first time the entire array of experimental data on single-crystalline samples of terbium, dysprosium and holmium have been analyzed, in which there is at least the slightest indication of the degree of chemical purity of the materials used. This information is absent in most works devoted to heavy REM. It should be also noted that in those papers where the purity of the rare earth metal is given, it is usually done without specifying the details of such analysis. An experiment carried out under the same conditions for samples containing different (controlled) amounts of impurities can be considered correct in this case.

That is why this paper compares the results obtained on samples with different degrees of chemical purity, time and methods of manufacturing, the properties of which were measured on different experimental equipment. These circumstances undoubtedly also affect the difference in properties. For an accurate quantitative analysis of the influence of chemical impurities on the properties of heavy REM, a unified approach is necessary, within which it is important to compare the properties of both highly pure and artificially doped with impurity atoms samples cut from the same single-crystalline sample. At the same time, it is obvious that measurements of certain properties should be carried out twice or thrice under the same experimental conditions. Improved purity of metals should allow more accurate experiments in future, but at the same time they are most likely to contribute less to human knowledge and understanding of REM properties than the work of the past 80 years.

#### **Declaration of Competing Interest**

The authors declare no conflict of interest.

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