STUDY OF THE MAGNETIC PROPERTIES OF THE RARE EARTH METAL-INDIUM SYSTEM AT HIGH TEMPERATURES

Shakarov Holik Ochilovich
Candidate of physical and mathematical sciences, associate professor. Samarkand State University. Department of General Physics. Uzbekistan.

Usarov Uktam Turatovich
Candidate of physical and mathematical sciences, associate professor. Samarkand State Architectural and Construction Institute. Department of Natural Sciences. Uzbekistan.

Annotation

The Faraday method was used to study for the first time the temperature dependence of the magnetic susceptibility $[\chi(T)]$ of rare earth metals (REM = Gd, Tb, Dy, Ho, Er, Tm) and their compounds with In in a wide temperature range of 20-1700^{0}C, covering the solid state, the melting process and the liquid state of these compounds. It was found that for all studied compounds, the χ (T) dependence, with the exception of compounds of the Gd-In system, obeys a linear law, and for compounds of the Gd-In system, the modified Curie-Weiss law, both in the solid and in the liquid states. The paramagnetic Curie temperature θ_P, the Curie-Weiss constant C, the temperature-independent component of the susceptibility χ_0, and the effective numbers of magnetic moments $\mu_{эфф}$ per REM atom were calculated from the $\chi^{-1}(T)$ (T) dependence of the compounds. It is shown that the paramagnetic states of the studied samples are satisfactorily described by the Van Vleck theory of paramagnetism. For the first time, the prediction of the theory of exchange interactions of the Ruderman-Kittel-Kasuya-Yosida type (RKKI) on the existence of a direct proportional dependence of the experimental values of θ_P on the de Gennes factor for the equiatomic compounds under study, similar to that of pure TREM, was confirmed semi-empirically. On the whole, it has been established that for the compounds of TREM with in, as in pure TREM, an exchange interaction of the RKKY type is characteristic.

Keywords: rare earth metal, magnetic susceptibility, magnetic moment, paramagnetic temperature, melting, liquid state, exchange interaction, de Gennes factor.

Introduction.

Quite a lot of experiments have been carried out to study the magnetic properties of pure REM at temperatures below 20^{0}C. Many works are devoted to the study of their magnetic properties in the solid paramagnetic state in the temperature range 20-1200^{0}C [1-4] and their compounds with non-magnetic metals, including indium (for example, P3M$_2$In [5], P3MIn[6], P3MIn$_3$ [7]) only in their magnetically ordered state, i.e. at temperatures below 20^0C. The results of these studies are summarized in reviews [4,8,9]. The number of works devoted to the study of the

magnetic properties of pure REM in the liquid state and their compounds with In above 20^0C is extremely limited [10-13]. It is of great scientific and practical interest to study the effect of weakly magnetic metals on the quantum state of $4f$ - REM electrons at high temperatures, covering their solid and liquid states. Such investigations are important for the development of the theory of the electronic structure and magnetism of REM compounds with weakly magnetic metals at high temperatures, covering their liquid state.

The aim of this work is to study the effect of a diamagnetic metal (indium) on the magnetic characteristics of the TREM (Gd, Tb, Dy, Ho, Er, Tm,) and to check the applicability of the Van Vleck theory of paramagnetism [14] and RKKI [15-19] for intermetallic compounds in binary systems TRZM – In, by measuring the dependence $\chi(T)$of these systems in a wide range of high temperatures, covering their solid state, melting process and liquid state. This article is a continuation and generalization of our research in this direction.

Results and its discussion

For the first time, we experimentally investigated the dependences χ (T) of TPM (REM = Gd, Tb, Dy, Ho, Er, Tm) and their compounds with indium in a wide temperature range (from room temperature to 1700^0C), covering the solid state, the melting process and the liquid state these objects.

When choosing the conditions for the synthesis of compounds and measuring their dependence $\chi(T)$, we used the state diagrams (DS) of the studied systems, constructed by us earlier [20-23]. The magnetic susceptibility was measured by the Faraday method using a high-temperature pendulum balance [23] in a sealed molybdenum crucible in an atmosphere of purified helium with excess pressure. The maximum relative measurement error did not exceed 3%.

Dependences $\chi^{-1}(T)$ for samples of binary systems Gd-In, Tb-In, Dy-In, Ho-In, Er-In, and Tm-In are shown in fig. 1. First of all, it should be noted that the measured values of the magnetic susceptibility are in good agreement with the experimental data of other authors for pure REM in the solid state [1-4], obtained at temperatures above 20^0C and for REM_2In compounds [5], REMIn [6] , $REMIn_3$ [7] obtained at temperatures of about 20^0C.

An analysis of fig. 1 shows that the $\chi^{-1}(T)$ polytherms for pure TPM and all studied compounds, with the exception of the samples of the Gd-In system, are linear. This indicates that the χ (T) dependences of these samples are described by the linear Curie-Weiss law:

$$\chi = \frac{C}{(T-\theta_P)} \qquad (1)$$

where C is the Curie-Weiss constant, θ_P-paramagnetic Curie temperature.

As can be seen from figure 1, a, for samples of the Gd-In system, the dependence$\chi^{-1}(T)$ are satisfactorily described by the modified Curie-Weiss law:

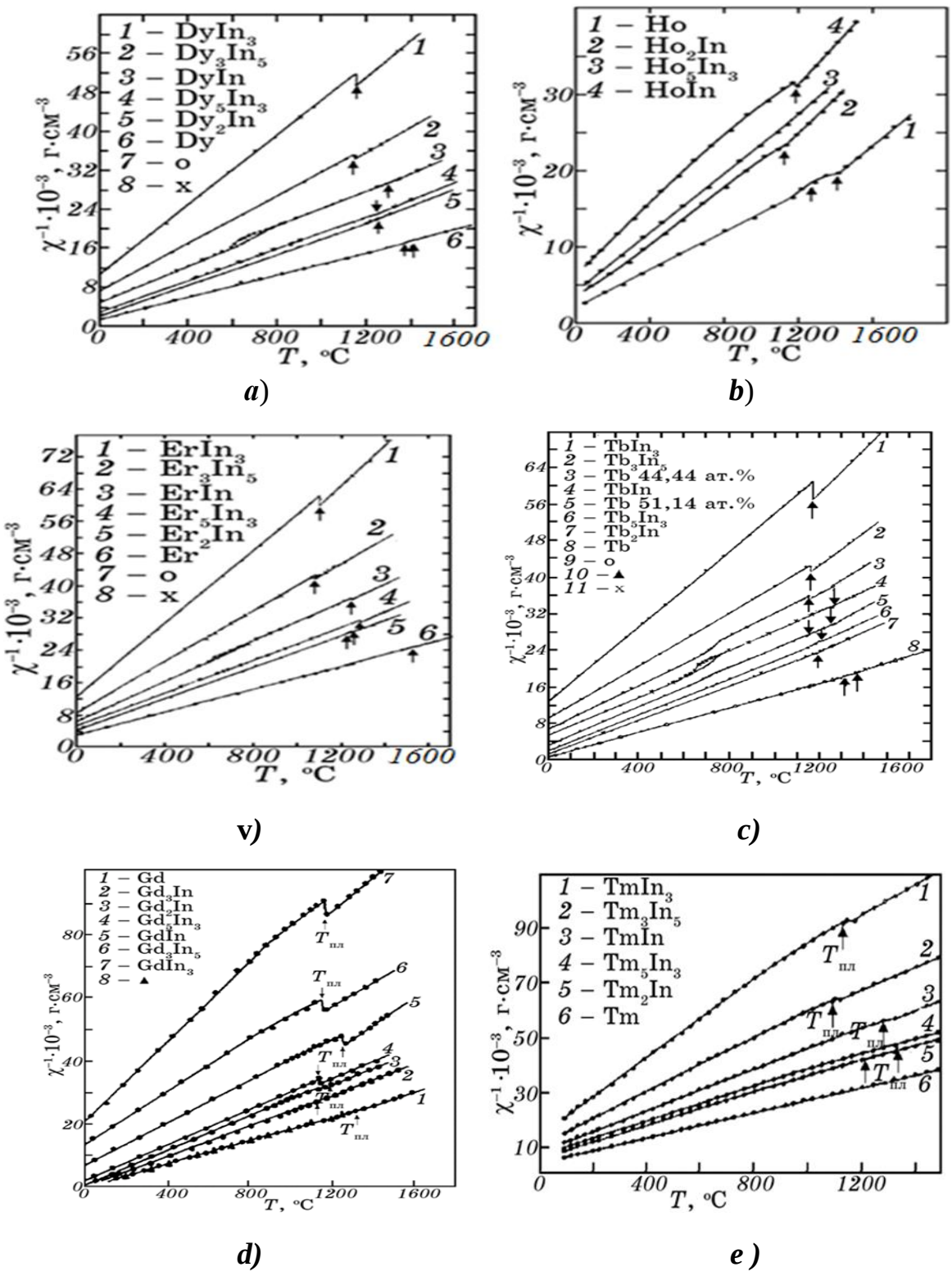

Fig. 1. Dependences $\chi^{-1}(T)$ for REM-In systems (REM = Gd, Tb, Dy, Ho, Er, Tm). 7 (a,v) and 9 (c) - data from [2]; 10 (c) and 7 (d) - data from [3] and [4], respectively; 11(c),8 (v)- measured on cooling.

$$\chi = \chi_0 + \frac{C}{(T-\theta_P)}, \qquad (2)$$

where χ_0– temperature-independent susceptibility term.

From figures 1, a), v) and c) it can be seen that the dependence $\chi^{-1}(T)$ compounds of equiatomic composition DyIn, ErIn and TbIn, thermal hysteresis is observed in the temperature range - 600-720^{0}C, despite the long (30-40 min) isothermal holdings between measurements. Apparently, this phenomenon is associated with the rearrangement of the crystal lattice of these compounds. According to the data of [11], TbIn undergoes a polymorphic transition at a temperature of about 900^{0}C, from a tetragonal modification to a high-temperature cubic one. This is an indirect proof of the reliability of our explanations for the cause of the observed thermal hysteresis.

It can be seen from the data in Fig. 1 that the melting process causes a break in the dependence $\chi^{-1}(T)$ for all samples except P3MIn, P3M$_3$In$_5$ and P3MIn$_5$, for which a weak jump is noted. This indicates that the energy state 4*f*– electrons in the studied objects during melting almost does not change.

It is known [15] that for most of the ions P3M^{3+} (with the exception of Sm^{3+} and Eu^{3+}), energy gap between the ground and first excited level of 4*f*-electrons ($\Delta E=E_{J+1}-E_J$) large compared to thermal energy (k_BT) at room temperature (the case of wide multiplets), and the population of the first excited level is small. In this case, within the framework of Van Vleck's theory of paramagnetism [14,15] for the dependence χ(T) the ensemble of free ions the following expression was obtained [15,24-26]:

$$\chi = \frac{N_A}{M}\frac{g_J^2\mu_B^2 J(J+1)}{3k_BT} + \frac{N_A}{M}\alpha_J, \qquad (3)$$

Where N_A – Avogadro's number, M – atomic mass of a given P3M, k_B – Boltzmann constant, μ_B – Bohr magneton,

$$g_J = 1 + \frac{S(S+1)+J(J+1)-L(L+1)}{2J(J+1)} \qquad (4)$$

- Lande factor,

$$\alpha_J = \frac{\mu_Б^2}{6(2J+1)}\left(\frac{F_{J+1}}{E_{J+1}-E_J} - \frac{F_J}{E_J-E_{J-1}}\right) \qquad (5)$$

at

$$F_J = J^{-1}[(S+L+1)^2 - J^2][J^2-(S-L)^2]. \qquad (6)$$

Here S, L and J are the quantum numbers of the ground state of electrons 4*f* - the layer of ions P3M^{3+}.

The first term in (3) describes the temperature-dependent component of the magnetic susceptibility, i.e. the contribution of $4f$ - electrons, and the second χ_0 – temperature-independent Van Vleck paramagnetism. After designation

$$\chi_0 = \frac{N_A \alpha_J}{M}, \quad C = \frac{N_A}{M} \frac{g_J^2 \mu_Б^2 J(J+1)}{3k_Б T} \qquad (7)$$

and replacing T with T – θ_P (i.e., taking into account the magnetic interaction of ions $РЗМ^{3+}$) from (3) the empirical expression of the modified Curie-Weiss law (2) is obtained, and at $\chi_0 = 0$ – expression of the linear Curie-Weiss law (1).

In the numerator of formula (7), for the theoretical value of the magnetic moment of a free ion, $РЗМ^{3+}$ (which can be derived from the vector model of the atom [15]):

$$\mu_J = g_J \sqrt{J(J+1)} \mu_Б . \qquad (8)$$

Taking into account (7) and (8), from expression (1) we find the formula for calculating the experimental values of the effective magnetic moments per ion $РЗМ^{3+}$:

$$\mu_{эфф} = \sqrt{\frac{3k_Б MC}{N_A \mu_Б^2}} = 2{,}83\sqrt{MC}\,\mu_Б. \qquad (9)$$

When one of the components of the binary compound (In) has no magnetic moment, then it is advisable to calculate the value μ_{eff}, per ion of the magnetic component ($РЗМ^{3+}$) by the following formula [27]:

$$\mu_{эфф} = 2{,}83\sqrt{C\left(M_1 + \frac{xM_2}{100 - x}\right)}\ \mu_Б, \qquad (10)$$

Where M_1 and M_2 – respectively, the atomic masses of REM and indium, x-content of indium in at.%.

The values χ_0 for samples of the Gd-In system, found by their dependence $\chi(1/T)$, are given in Table 1. It should be noted that χ_0 does not significantly affect the linear nature of the dependence $\chi^{-1}(T)$ (fig. 1, a) samples of the system Gd-In.

Table 1.

Sample	Gd	Gd_3In	Gd_2In	Gd_5In_3	GdIn	Gd_3In_5	$GdIn_3$
$\chi_0, 10^{-6}$ г · см$^{-3}$	7,5	1,2	1,8	3,0	7,2	8,9	10,7

Construction and analysis of experimental dependencies $\chi(1/T)$ it was found that for all studied samples of systems РЗМ-In, except for samples of the Gd-In system, values χ_0 negligible.

Least-squares dependency processing $\chi^{-1}(T)$ samples of binary systems (Gd, Tb, Dy, Ho, Er, Tm) - In, the values θ_P, C и μ_{eff}. The calculation results are shown in fig. 2. Experimental values μ_{eff}, found by (10), both for the solid and liquid states of the samples, are very close to the theoretical values μ_J, calculated according to (8), equal to 7.92, 9.72, 10.64, 10.60, 9.58, and 7.57 (in units.$\mu_Б$) , respectively for free ions Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+}.

The values μ_{eff} for solid and liquid states differ little from each other. This indicates that the diamagnetic metal indium and high temperature ($T \approx 2000$ K) almost does not change the number and degree of localization of electrons in 4f-shells at the sites of the crystal sublattices of the studied compounds. The energy state of these electrons in the studied compounds remains the same degree as in pure HREM, even very close as in free $HREM^{3+}$.

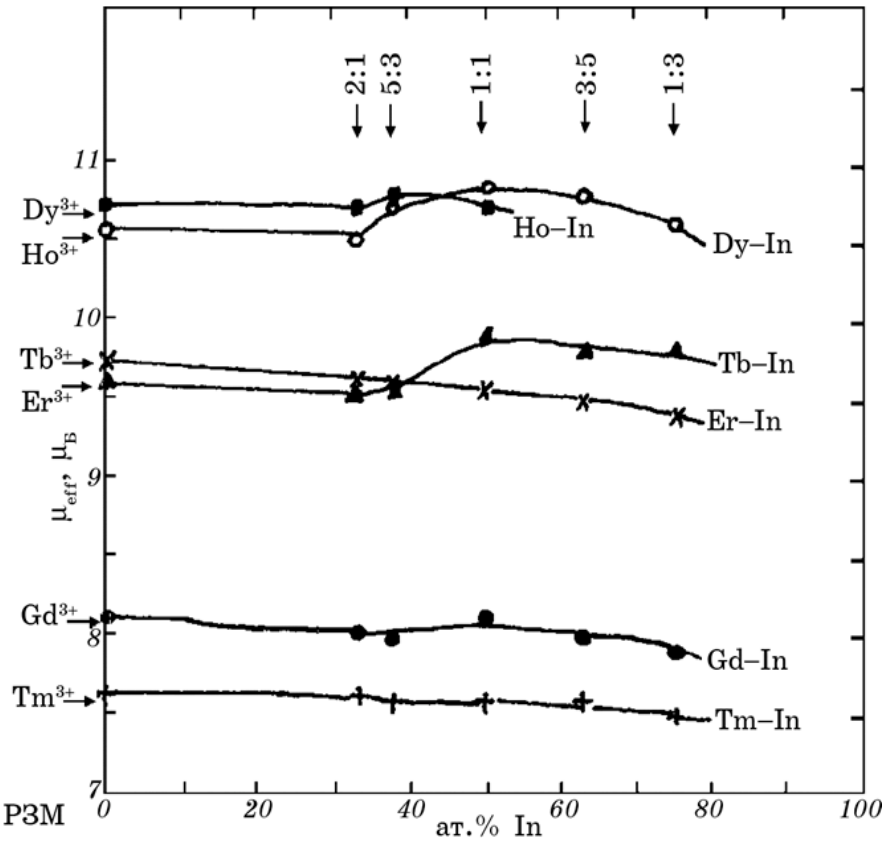

Fig. 2. Concentration dependence of the value μ_{eff} for HREM-In system.

All this indicates that 4f - electrons, predominantly responsible for the paramagnetism of the studied compounds, are protected from external influences almost to the same extent as in pure HREM. In other words, in the indicated objects 4f - electrons lie deep under $5s^2 5p^6$ - shell of ions $HREM^{3+}$. The energy states of 4f - electrons in these compounds quite well correspond to the ground state of 4f - electrons of free ions $HP3M^{3+}$ both in solid and liquid states. The configuration and quantum number J of these electrons in the indicated objects does not change during the transition from solid to liquid state.

Within the framework of the RKKY theory [15-19] using the molecular field representation to explain the experimental values θ_p REM obtained the following expression [15,19,28,29]:

$$\theta_p = \frac{3\pi n^2}{k_B \Omega^2 E_F} A_{sf}^2(0) G \sum_{n \neq m} F\left(2\vec{k}_F \left|\vec{R}_n - \vec{R}_m\right|\right), \qquad (11)$$

where n is the number of conduction electrons per atom; Ω - atomic volume; $A_{sf}(0)$ – integral $s-f-$ exchange interaction, independent of $\vec{k}_F$; E_F and $\vec{k}_F$ – energy and wave vector at the Fermi surface; $\left|\vec{R}_n-\vec{R}_m\right|$ - the distance between the magnetic ions of rare-earth metals located at the sites of the crystal lattice n and m; $F\left(2\vec{k}_F\left|\vec{R}_n-\vec{R}_m\right|\right)=F(y)$ – Ruderman-Kittel function, defined by the expression

$$F(y)=(y\cos y-\sin y)/y^4\,; \tag{12}$$

$$G=(g_J-1)^2 J(J+1) \tag{13}$$

– de Gennes factor [29] for REM. In (13) g_J – Lande factor - is determined by the following expression:

$$g_J=1+[J(J+1)+S(S+1)-L(L+1)]/2J(J+1), \tag{14}$$

where S, L u J – respectively, the total values of the quantum numbers of the spin, orbital, and total mechanical moments of electrons in the 4f layer.

Within the framework of the RKKY theory, the following expression was obtained to calculate the integral of the indirect exchange interaction [15,19]:

$$A=\frac{9\pi n^2}{E_F\Omega^2}A^2{}_{sf}(0)\sum_{n\neq m}F\left(2\vec{k}_F\left|\vec{R}_n-\vec{R}_M\right|\right). \tag{15}$$

Taking into account (15) and (13), from expression (11) a proportional dependence of the value θ_p for pure REM from their de Genne factor:

$$\theta_p=\frac{A}{3k_Б}(g_J-1)^2 J(J+1). \tag{16}$$

The de Gennes factor for the studied compounds can be calculated according to the additivity rule:

$$G=(1-x)G_{REM}+xG_{In}\,, \tag{17}$$

where $x-$content In in atomic fractions; G_{REM} and $G_{In}-$ respectively, the de Gennes factors for REM and In. Since the term of the ground state of the trivalent ion In $-{}^1S_0$, so $G_{In}=0$. Taking into account this fact and (17), for the value θ_P of the studied compounds we find:

$$\theta_P=\frac{A}{k_Б}(1-x)(g_J-1)^2 J(J+1) \tag{18}$$

The outer electron shell of trivalent REM ions is practically the same ($5s^25p^6$), moreover, they are located in the nodes of the crystal hexagonal lattice, which almost does not change when going from one metal to another. The indirect exchange integral according to (15) depends on n, $A_{sf}(0)$, Ω, E_F and lattice sums (function $F(y)$). All these values can be considered constant in the first approximation [30]. From expression (18) it follows that the

values θ_p for the studied compounds should be proportional to the de Gennes factor, similar to that of pure REM. Thus, expression (18) makes it possible to semi-empirically verify this prediction of the RKKY theory.

It was noted above that the experimental values of the effective numbers of magnetic moments per one heavy ion REM^{3+}, in all studied heavy rare-earth metals and compounds with indium satisfactorily correspond to the theoretical values of free ions of heavy rare-earth metals $^{3+}$. Consequently, the energy interval between the ground level and the first excited level of 4f electrons is large compared to $k_БT$, and the population of the excited level is very small. Therefore, when calculating G for heavy REM and compounds under study, the values J and g_J for the main levels of free ions of heavy REM^{3+} [Gd^{3+} ($J=7/2$, $g_J=2$); Tb^{3+} ($J=6$, $g_J=3/2$); Dy^{3+}($J=15/2$, $g_J=4/3$); Ho^{3+}($J=8$, $g_J=5/4$); Er^{3+}($J=15/2$, $g_J=6/5$); Tm^{3+}($J=6$, $g_J=7/6$)].

The results of calculations by (16) and (18) are shown, respectively, in Fig. 3. Analysis of fig. 3 shows that the dependencies $\theta_p(G)$ for the studied equiatomic compounds (curves 2-5) also have an almost linear character and satisfactorily correspond to the linear character of the dependence $\theta_p(G)$ for heavy rare earth metals (curve 1). Hence the change θ_p in the compounds under study is quite close to what the RKKY theory predicts. This indicates that the exchange interaction in the studied compounds is an interaction of the RKKY type, as in pure heavy REM

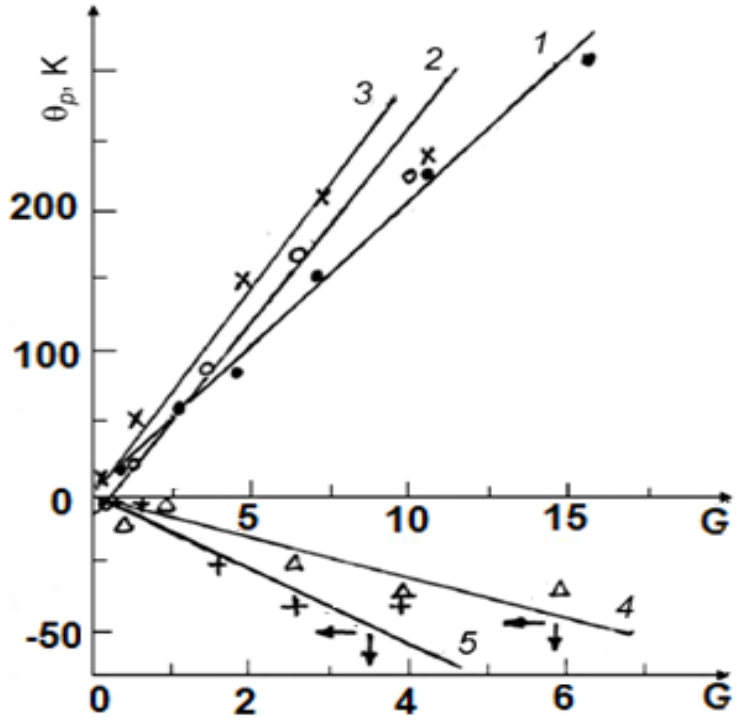

Fig. 3. Dependencies $\theta_P(G)$ for the studied samples.
$Cur.1-\ REM\ (REM=Gd,Tb,Dy,Ho,Er,Tm);\ cur.2-\ REM_5In_3;$
$cur.3-\ REM_2In;\ cur.4-REM_3In_5;\ cur.5.-REMIn_3.$

Conclusions

Based on the results obtained, the following conclusions can be drawn:

1. For the first time measured the dependence $\chi(T)$ pure TRPM (Gd, Tb, Dy, Ho, Er, Tm) in a wide temperature range of 20-1700^{0}C, covering their solid state, melting process and liquid state. It was found that the dependence $\chi(T)$ for samples of the Gd-In system it is described by a modified law, and for other compounds - by the linear Curie-Weiss law.

2. By dependence $\chi^{-1}(T)$ determined the main magnetic characteristics of the studied objects -C, θ_P and μ_{eff}. The quantity μ_{eff}, both for the solid and for the liquid state of the samples is close to their theoretical value of free ions HREM^{3+}. This indicates that the non-magnetic environment (indium) and high temperature (≈2000K) have almost no effect on the quantum state of 4f - electrons in pure TREM. Ions HREM^{3+} in the condensed state of the studied objects behave almost like free ions, and their paramagnetic state is satisfactorily described by the Van Vleck theory of paramagnetism for triply charged free ions

3. For the first time, semi-empirical research has confirmed the prediction of the RKKY theory, i.e. the same proportional relationship was established between the experimental value of the paramagnetic Curie temperatures and the de Gennes factor for equiatomic compounds of HREM with indium, similar to that for pure HREM. On the whole, it was found that for all the studied intermetallic compounds in the REM-In system, as well as for pure HREM, the exchange interaction of the RKKY type is characteristic.

REFERENCES

1. Arajs S., Miller D.S. //J.Appl.Phys. - 1960. - V.31. - No.5. - P.3255-3265.
2. Arajs S., Colvin R.V. //J.Appl. Phys. - 1961. - V.32. - No.3. - P.336S-337S.
3. Muller M. Huber E, Guntherodt H.J. //J.de Phys. - 1979. - T.40. - Suppl No.5. - P.C5-260-C5-261.
4. Arazhs S., Kolvin R.V. // New research on rare earth metals. M .: Mir, 1964 .-- p. 100-135.
5. Gameri-Seale H., Anagnostopuls T., Vakinhos T.R. //J.Appl Phys. - 1979. - V. 50. No.1. - P.434-437.
6. Lethuillier P., Percheron-Gougen A. // J. Less. Com. Met. - 1976. - V.46. - P.85-89.

7. Buschow K. H. J., De Wijn H. W., Van Diepen A. M. // J. Chem. Phys. - 1969. - V. 50. - No.1. - P.137-141.
8. Taylor K. Intermetallic compounds of rare earth metals. - M .: Mir, 1974 .-- 224 p.
9. Bushov K.H. J./Rep.Prog.Phys. - 1979. - V.42. - No.8. - P.1373.
10. Aluf A.A., Shakarov Kh.O., Semyannikov A.A. Yatsenko S.P.// Izv. Non-ferrous metallurgy. - 1989. - No. 5. - pp. 90-93.
11. Kuvandikov O.K., Shakarov Kh.O. // DAN UzSSR. -1987. - Number 3. - p. 34- 36.
12. Shakarov Kh.O. // Izvestiya vuzov. Physics. - 2004. - No. 12. - p. 7-10.
13. Shakarov Kh.O.// News of universities. Physics. - 2005. - No. 1. - p.88-89.
14. Van Vleck. The Theory of Electric and Magnetic Susceptibilities. –Oxford Univ.Press, 1932. - 384 p.
15. Vonsovsky S.V. Magnetism - M.: Nauka, 1971.-1032 p.
16. Ruderman M. A., Kuttel C. // Phys. Rev.-1954.-V.96.- No.1.- P. 99-102.
17. Kasuya T. A. // Prog. Theor. Phys. (Kyoto). 1956.-V. 16.- No.1.-P. 45-57.
18. Yosida K. // Phys. Rev.-1957.-V106.- No.5.- P. 893-898.
19. Taylor K. Intermetallic compounds of rare earth metals. - M.: Mir. 1974 - 224 p
20. Shakarov Kh.O., Semyannikov A.A., Yatsenko S.P., Kuvandikov O.K. // Izd. Of the Academy of Sciences of the USSR. Metals. - 1981. - No. 2. - p. 243-246.
21. Kuvandikov O.K., Shakarov Kh.O., Yatsenko S.P., Semyannikov A.A., Saidov M.S. // DAN UzSSR. –1981. - No. 2. - p. 28-30.
22. Yatsenko S.P., Semyannikov A.A., Shakarov H.O., Fedorova E.G. //J.Less.Comm.Met. - 1983. - V.90. - No.1. - p. 95-108.
23. Kuvandikov O.K., Shakarov Kh.O. Structural and magnetic properties of compounds of rare earth metals with normal and transition metals at high temperatures. –T.: "Fan and technology", 2017. -308s.
24. Selwood P. Magnetochemistry. -M.: IL, 1958 - 460 p.
25. Krinchik S.G. Physics of magnetic phenomena. -M.: Publishing house of Moscow State University, 1976-367 p.
26. Taylor K., Darby M. Physics of rare earth compounds. M.: Mir, 1974. -374 p.

27. Antropov V.A., Radovskiy I.Z., Davgopol S.P., Geld P.V. // UFZh 1976. -T.21. - Number 3. -s. 360-363.
28. Rocher Y.A. // Phys. Chem. Sol.-1962.-V. 23.-P. 1621-1629.
29. De Gennes, P. G. // Compt. Rend. -1958.-V.247.- P.1836-1838.
30. Nikitin S.A. // ZhETF. - 1979. -T.77. - issue 1. - p. 343-351.