

Magnetic and magneto-optical properties of oxide glasses containing Pr^{3+} , Dy^{3+} and Nd^{3+} ions

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Abstract

Magnetization of a number of oxide glasses containing Pr^{3+} , Dy^{3+} and Nd^{3+} ions has been measured as a function of the magnetic field (0–50 kOe) and temperature (5–300 K). Magneto-optical Faraday rotation (FR) in the same glasses has been measured as a function of the light wavelength (240–1000 nm) and temperature (80–350 K). Dispersion of FR has permitted us to find the positions of the effective transitions responsible for FR and their magneto-optical activities. Temperature dependencies of both FR and the magnetization at high temperatures obey the Curie–Weiss law with negative Weiss constants. High temperature magnetic moments of the rare-earth ions in the glasses are rather close to those of the free ions. At low temperatures, all studied glasses reveal downward curvature of the reciprocal magnetization variation with decreasing temperature. The origin of this behavior is discussed. Formation of antiferromagnetically ordered clusters in Dy glasses is supposed.

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1. Introduction

Investigation of glasses activated by rare-earth (RE) elements is of interest due to the possibility of their application in optically pumped solid state lasers, optical modulators, switches, and so forth. Optical properties of $4f-4f$ and $4f-5d$ transitions

and their dependence on RE ions environment in glasses are also interesting from the fundamental point of view and were studied in a great number of works (see, e.g., Refs. [1–3] and references therein). Magneto-optical properties of glasses are studied over a rather long period of time, but not so extensively and mainly in connection with allowed $4f-5d$ transitions (e.g., Refs. [4–13]). Magneto-optical properties of RE compounds are closely connected with their magnetic properties. This connection was first considered by Van

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Vleck and Hebb [14]. Magnetic properties of RE compounds are studied experimentally and theoretically for a long time. However, investigations of magnetic properties of RE doped glasses have begun not long ago. They are devoted to the study of magnetic susceptibility [15–21] and electron paramagnetic resonance [22,23]. The study of glasses containing RE ions is interesting not due to their direct practical importance alone. Variation of RE ion concentration permits to study collective phenomena of different kinds and cluster formation, in particular. The study of nanostructures such as clusters, quantum dots and holes is now widespread and is connected with the hope of creating of new materials for microelectronics.

In the present work, we study temperature dependencies of the optical Faraday rotation (FR) and of the magnetic susceptibility of several RE containing glasses, which were not subjected to such study before. These glasses differ from one another not only in the type of RE ions but also in their concentration and in composition of the glass matrixes. The results are analyzed from the viewpoint of contribution of separate RE ions and possible clusters of bound RE ions into the observed properties.

2. Experimental

Glass compositions and RE ion concentrations according to the initial components are presented

in Table 1. The concentration of RE ions per volume was calculated from the glass densities and compositions. The sample designations used in Table 1 were chosen to be consistent with the glass sample designations presented in our previous paper devoted to glasses activated with RE ions [3].

Glasses Dy1 and (Dy5–Dy8) were prepared from the corresponding oxides as starting materials. La_2O_3 was added in glasses Dy5–Dy8 so that the total molar concentration of $(\text{Dy}_2\text{O}_3\text{--La}_2\text{O}_3)$ was 25%. The Dy_2O_3 concentrations were 2.5, 12.5, 17.5, and 22.5 mol% for Dy5–Dy8, respectively. Glasses containing praseodymium and neodymium were prepared from the mixture of reagents H_3PO_4 , SiO_2 , GeO_2 and appropriate RE oxides (for samples Nd, Pr1 and Pr5) or $\text{Li}_2\text{B}_4\text{O}_7$, B_2O_3 and Pr_6O_{11} (for samples Pr3 and Pr4). The samples Nd, Pr1, Pr5, and Dy5–Dy8 were made in a resistance furnace in quartz or platinum crucibles 100 ml in volume at 1300–1500°C. To make the samples of Pr3 and Pr4, 40 g batches were placed into a carbon crucible and heated at $1100 \pm 50^\circ\text{C}$ in the Ar gas. During this process, Pr^{4+} from the compound with the mixed valency was reduced to Pr^{3+} , so that the final glass composition can be described by the formula $\text{LiB}_3\text{O}_5 + x\text{Pr}_2\text{O}_3$. The melts were vitrified by rapid cooling to 350–400°C, and then the glasses obtained were annealed at 300°C. The total impurity levels in all samples were 0.12 mass% of Pr_6O_{11} , 2×10^{-3} mass% of other R_2O_3 , and 10^{-4} mass% of other uncontrolled impurities.

Table 1
Glass compositions

Sample design	RE ion	Matrix composition	Conc. of RE oxide (mass %)	Conc. of RE ion (10^{21} cm^{-3})
Nd	Nd^{3+}	$20\text{Nd}_2\text{O}_3 + 60\text{P}_2\text{O}_5 + 10\text{SiO}_2 + 10\text{GeO}_2$	39.8	5.38
Dy1	Dy^{3+}	$15\text{Dy}_2\text{O}_3 + 60\text{P}_2\text{O}_5 + 15\text{SiO}_2 + 10\text{GeO}_2$	34.82	3.55
Dy5	Dy^{3+}	$\text{Dy}_2\text{O}_3\text{--La}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2\text{--GeO}_2$	2.65	0.37
Dy6	Dy^{3+}	$\text{Dy}_2\text{O}_3\text{--La}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2\text{--GeO}_2$	32.2	3.64
Dy7	Dy^{3+}	$\text{Dy}_2\text{O}_3\text{--La}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2\text{--GeO}_2$	44.3	5.28
Dy8	Dy^{3+}	$\text{Dy}_2\text{O}_3\text{--La}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2\text{--GeO}_2$	56.1	6.96
Pr1	Pr^{3+}	$20\text{Pr}_2\text{O}_3 + 60\text{P}_2\text{O}_5 + 20(\text{SiO}_2\text{--GeO}_2)$	39.3	5.02
Pr3	Pr^{3+}	$6 \text{ Pr}_2\text{O}_3 + 94 \text{ LiB}_3\text{O}_5$	15	1.37
Pr4	Pr^{3+}	$13.4 \text{ Pr}_2\text{O}_3 + 86.6 \text{ LiB}_3\text{O}_5$	30	3.27
Pr5	Pr^{3+}	$25\text{Pr}_2\text{O}_3 + 75\text{P}_2\text{O}_5$	43.6	5.29

The FR measurements were made on polished glass samples of thickness ranging from 0.2 to 1.1 mm. For the magnetic measurements, bulk glass samples of $4 \times 4 \times 2 \text{ mm}^3$ were used.

FR measurements were made by the null-analyzer method (with modulation of the light polarization plane) in a wavelength range of 240–1000 nm and in a temperature range of 80–350 K, using the original spectropolarimeter. The accuracy of FR measurements was $\pm 0.2 \text{ min}$. The magnetic field changed from -5 to $+5 \text{ kOe}$, with an accuracy of $\pm 10 \text{ Oe}$.

Measurements of magnetization were performed using a commercial SQUID magnetometer (Quantum Design MPMS-55) with a scan length of 4 cm.

3. Results and discussion

3.1. Magneto-optical properties of the glasses

FR of the plane polarization of light in material is given by the equation:

$$\alpha = V l H, \quad (1)$$

where α is the rotation angle, l is the length of the light path in the medium, H is the magnetic field applied along the light beam, and V is the Verdet constant. In general, the Verdet constant consists of three terms [24,25]:

$$V = A(\lambda) + B(\lambda) + C(\lambda, T). \quad (2)$$

The diamagnetic term A is proportional to the splitting of electronic states in the magnetic field and does not depend on temperature T . The paramagnetic term C is proportional to the difference of the thermal populations of components of the ground state splitting in the magnetic field, and therefore it depends on temperature. The term B is called paramagnetic as well. It is due to the mixing of states by the magnetic field, and therefore it does not depend on temperature (in a limited temperature range). This term exists only in the condensed matter, when the ligand field splitting of states takes place [26]. Both paramagnetic terms have identical dispersion (λ is the light wavelength), different from the dispersion of the diamagnetic term.

Van Vleck and Hebb [14] derived the following relationship between the paramagnetic Verdet constant (C -term) and the magnetic susceptibility χ for a free ion:

$$V = \chi K_0 g^{-1} [1 - (\lambda^2/\lambda_0^2)]^{-1} \equiv C_0 [1 - (\lambda^2/\lambda_0^2)]^{-1}, \quad (3)$$

where g is the Lande factor of the ground state splitting, λ_0 is the wavelength of the effective electron transition equivalent in action to all transitions, causing the FR far enough from the resonance absorption and K_0 is a coefficient of proportionality between the magneto-optical activity of the effective transition, C_0 , and the susceptibility. The experimental dependencies of FR in the studied glasses, obtained at $T = 85$ and 300 K , follow the dispersion described in Eq. (3) quite well, if one does not take into account features connected with f–f transitions. Some of these dependencies are shown in Fig. 1. The effective wavelengths, λ_0 , are determined from the experimental dispersions according to Eq. (3), and they are given in Table 2. Dieke and Crosswhite [27] have calculated the approximate wavelengths of the 4f–5d transitions, which are supposed to be responsible for FR. They are 172.4, 119, and 188.6 nm for Nd, Dy, and Pr, respectively. Energies of these transitions in condensed matter are usually smaller than in free ions.

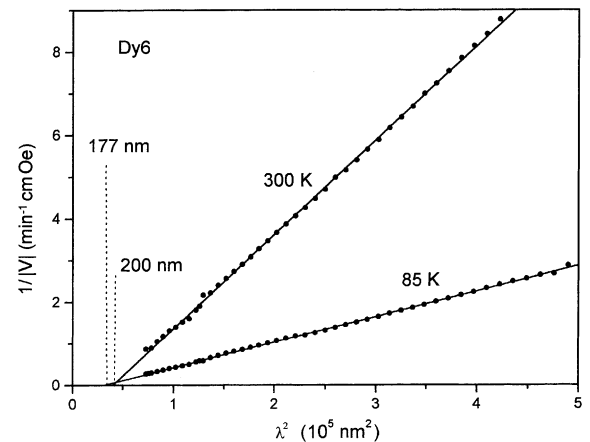


Fig. 1. Reciprocal Verdet constant of Dy6 glass as a function of the light wavelength at two temperatures.

Table 2
Magneto-optical properties of the glasses

Sample	Nd	Dy1	Dy6	Dy7	Dy8	Pr1	Pr3	Pr4	Pr5
$\lambda_0(85)$	200 ± 5	171 ± 1	177 ± 1	179 ± 1	187 ± 1	170 ± 1	180 ± 1	193 ± 1	170 ± 1
$\lambda_0(300)$	200 ± 5	181 ± 1	200 ± 1	189 ± 1	183 ± 1	178 ± 1	206 ± 1	210 ± 1	175 ± 1
C_0	1.2	4.1	3.1	3.5	3.9	3.4	1.9	2	4.1
θ	-25 ± 3 (-8)	-4 ± 3	-3 ± 3	-8 ± 3	-8 ± 3	-41 ± 3 (-37)	-11 ± 3 (-11)	-27 ± 3 (-19)	-43 ± 3 (-43)

λ_0 (nm) is the position of the effective absorption band responsible for the FR at $T = 85$ and 300 K; C_0 (10^{-22} min cm² Oe⁻¹ ion⁻¹) is the magneto-optical activity of the effective absorption band at $T = 300$ K; θ (K) is the paramagnetic Neel temperature, determined from the temperature dependencies of FR (see comments in the text).

So, this transition in Pr³⁺ has been observed at 225 nm in bromide complex in ethanol solution and at 215 nm in aqua complex in ethanol [28]. Berger et al. [6] have found from FR dispersion that in phosphate glasses this transition is positioned at 210 nm in Pr³⁺ and at 175 nm in Dy³⁺. Together with the data of Table 2 it is seen that the energy of this transition depends on environment of RE ions and only slightly depends on concentration of the RE ions and on temperature of the glasses. Paramagnetic magneto-optical activity, C_0 , per ion was found at $T = 300$ K from measured Verdet constants with the help of formula (3), and by using determined values of λ_0 . From Table 2 it is seen that magneto-optical activity weakly depends on the concentration of the RE ion (in the same matrix), appreciably depends on the matrix (with the same RE ion), and, naturally, strongly depends on the type of RE ion (see also Refs. [5,7]).

Thus, the parameters K_0 , λ_0 , and g are different for the different RE ions and for different materials in which RE ions are embedded. Therefore, there should not be a strict proportionality between the paramagnetic Verdet constant and the paramagnetic susceptibility of different materials. However, VanVleck and Hebb [14] have shown that temperature dependencies of these parameters for RE ions can be similar even when they are in compounds (ligand field acts) and even when exchange interaction between RE ions takes place. If this is indeed so, then experimental temperature dependencies of the reciprocal Verdet constants (see some of them in Fig. 2) show that the magnetic susceptibility obeys the Curie–Weiss law at high temperatures. When the paramagnetic

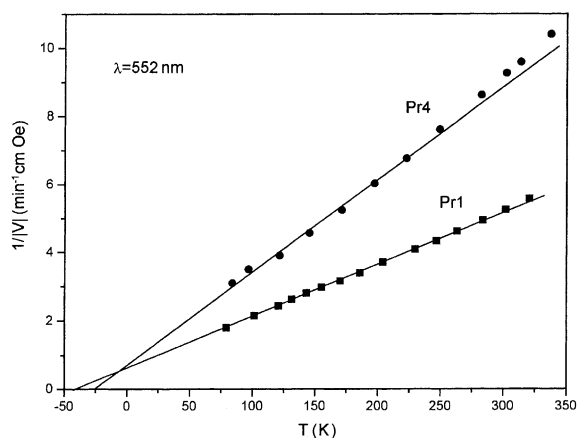


Fig. 2. Reciprocal Verdet constant of Pr glasses as a function of temperature at a light wavelength of 552 nm.

term C exists, it is usually much larger than the A and B terms up to room temperature. Far from the resonance, responsible for FR, A and C terms relate as $\sim 2kT/h\nu_0$, where ν_0 is the resonance frequency. At $T = 300$ K and $\nu_0 = 50000$ cm⁻¹ ($\lambda_0 = 200$ nm) this ratio is $\approx 0.8 \times 10^{-2}$. The relative value of term B cannot be estimated in general case, but usually it is also much smaller than the term C at not very high temperatures. In the glasses studied, in addition to the effects connected with the RE ions and described in Eq. (2), there is also a purely diamagnetic effect due to the glass matrix. This contribution did not comprise more than 5–8% of the negative paramagnetic FR observed in the studied glasses. The relative contribution of the temperature-independent A and B terms, as well as of the diamagnetic glass matrix, to the total FR increases

with a rise in temperature and this distorts the linear temperature dependence of the reciprocal FR. We tried to avoid this effect and used a lower part of the temperature dependencies (80–200 K) for the linear approximations. Paramagnetic Neel temperatures, determined in this manner from figures, such as Fig. 2, are shown in Table 2. The results obtained with the use of the total temperature interval are also provided for some glasses (in parenthesis). The difference in some cases is substantial.

3.2. Magnetic properties of the glasses

Magnetization curves of the glasses at $T = 5\text{ K}$ are depicted in Figs. 3 and 4. None of the samples reveal a hysteresis. Temperature dependencies of the reciprocal magnetization of some representative glasses at $H = 2\text{ kOe}$ are shown in Fig. 5. As in the case of FR, they display the Curie–Weiss type of magnetic behavior at high temperatures. Paramagnetic Neel temperatures, determined directly from the experimental curves, θ_1 , are given in Table 3. In some cases they differ from those determined from FR measurements (Table 2). In Fig. 5, there are also shown results of the FR measurements, normalized to the magnetization at $T = 300\text{ K}$. It is seen that usually temperature dependencies of magnetization and FR are indeed similar.

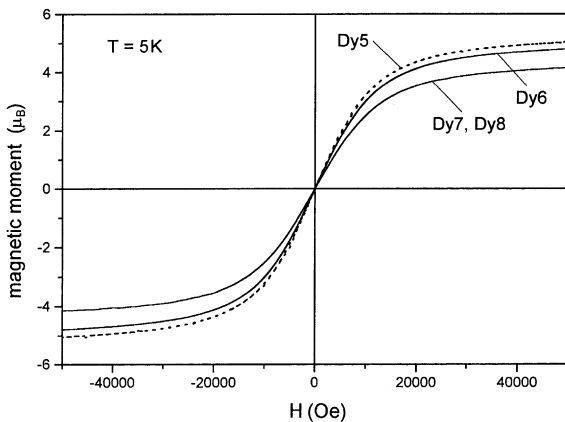


Fig. 3. Magnetization curves of Dy glasses (magnetization per ion of Dy).

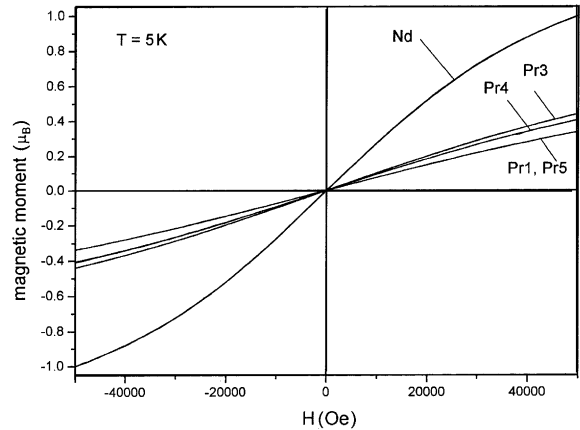


Fig. 4. Magnetization curves of Pr and Nd glasses (magnetization per RE ion).

The origin of the Curie–Weiss-type magnetic behavior of RE compounds can be different. For example, it can be due to the influence of crystal field or it can testify to antiferromagnetic ordering. We shall consider both of these variants. The possibility of magnetic ordering of amorphous materials was first shown by Gubanov [29]. The average reciprocal magnetization of disordered antiferromagnets changes slowly at $T < \theta$. However, all studied glasses reveal downward curvature of the reciprocal magnetization variation with decreasing temperature. In diluted magnetic compounds, it is possible to explain such behavior by the existence of isolated non-interacting ions simultaneously with clusters of magnetically coupled ions [30,31]. In this case, the magnetization of the glasses can be described by the formula:

$$M = AH/T + BH/(T - \theta). \tag{4}$$

Here

$$A = n_A m_{\text{eff}}^2 / 3k, \quad B = n_B m_{\text{eff}}^2 / 3k. \tag{5}$$

The first term in Eq. (4) corresponds to the isolated ions and the second one to the antiferromagnetic clusters. Designations in Eqs. (4) and (5) are the following: θ (negative value) is the Weiss constant or the paramagnetic Neel temperature; H is the external magnetic field; n_A and n_B are the

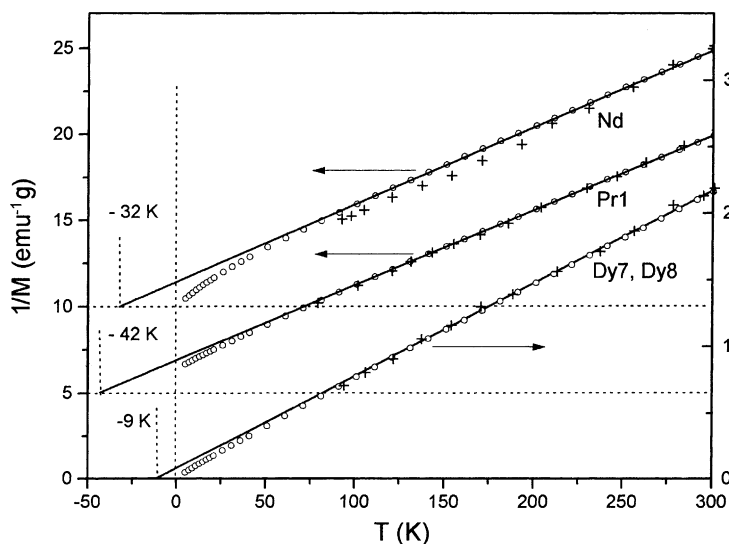


Fig. 5. Circles—reciprocal magnetization of some representative glasses at $H = 2 \text{ kOe}$ (magnetization per gram of RE atoms). Crosses—reciprocal FR normalized to the magnetization at $T = 300 \text{ K}$.

Table 3
Magnetic properties of the glasses

Sample	A	B	K	θ_1	θ_2	m_{eff}	$\chi(5)/\chi(300)$
Nd	5.1	6	0.55	-32 ± 2	-70 ± 5	3.5	31.9
Dy5	66	19	0.22	-7 ± 3	-35 ± 4	10.3	51.5
Dy6	62.5	19	0.23	-7 ± 2	-34 ± 3	10.1	49.1
Dy7	51	20	0.28	-10 ± 2	-42 ± 3	9.45	46.8
Dy8	50	21	0.3	-9 ± 2	-35 ± 3	9.45	45.8
Pr1	0.4	10.8	0.96	-42 ± 2	-42 ± 2	3.5	8.92
Pr3	0.75	10	0.93	-25 ± 2	-25 ± 2	3.42	12.3
Pr4	0.7	9.5	0.93	-29 ± 2	-29 ± 2	3.34	12.0
Pr5	0.4	10.8	0.96	-39 ± 2	-38 ± 2	3.5	8.95

A and B ($\text{emu K g}^{-1} \text{ kOe}^{-1}$) are parameters from Eq. (4); $K = B/(A + B)$; θ_1 and θ_2 (K) are paramagnetic Neel temperatures determined by different methods (see the text); $m_{\text{eff}}(\mu_B)$ is the effective magnetic moment of the ions in the high temperature region; $\chi(5)$ and $\chi(300)$ are low field magnetic susceptibilities at temperatures 5 and 300 K, respectively.

numbers of the isolated ions and ions in the clusters in 1 g of the RE element in the glass, respectively. The effective magnetic moment of one RE ion, m_{eff} , is supposed to be identical both for isolated ions and ions in the clusters at temperatures exceeding the paramagnetic Neel temperature of the clusters. The first term in Eq. (4) is valid when

$$\mu_B g J_{\text{eff}} H \ll kT. \quad (6)$$

The second term is usually valid when $T > |\theta|$. In Fig. 6, we present two variants of the function $1/M$, corresponding to Eq. (4) with $\theta = -20 \text{ K}$: F1, when $AH = BH = 0.5$ (equal number of separate RE ions and the ions in the clusters), and F2, when $AH = 0.1$ and $BH = 0.9$ (small relative number of the separate RE ions). In both cases, the function is linear enough when $T > |\theta| = 20 \text{ K}$. However, the point of the intersection of the line extrapolation of the function

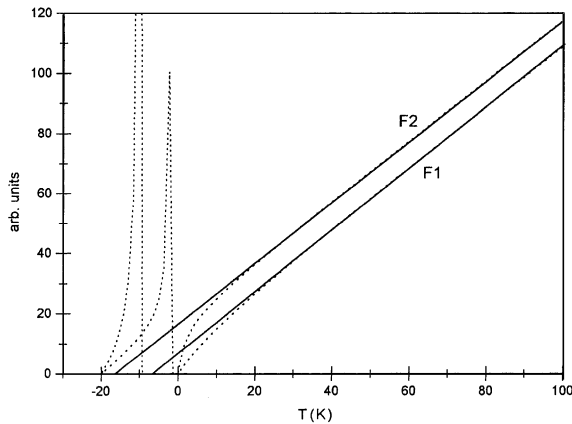


Fig. 6. Theoretical curves of reciprocal magnetization of glasses, containing both single RE ions and antiferromagnetic clusters with the paramagnetic Neel temperature of $\theta = -20$ K. See comments in the text.

$1/M(T)$ with the T axis, θ_1 , determined from the diagrams in Fig. 6, depends strongly on the ratio of numbers of the isolated ions and the ions in the clusters and does not correspond to the paramagnetic Neel temperature, θ , of the clusters. In particular, we find $\theta_1 = -6$ K from F1 and $\theta_1 = -16.5$ K from F2, while θ is assumed to be -20 K in both cases. Thus, the small values of θ found directly from the experimental diagrams (see, e.g., θ_1 for Dy glasses in Table 3) can, in some cases, be a consequence of a small number of the clusters.

When $T \rightarrow 0$, but condition (6) is still fulfilled, even a small amount of the single ions can make a substantial contribution to the magnetization (see Eq. (4)). Therefore, the total reciprocal magnetization can decrease when $T < |\theta|$ (Fig. 5), instead of increasing, as it does in antiferromagnets. At the lowest temperature of measurements, $T = 5$ K, and up to the field $H = 2$ kOe, in which temperature dependencies of magnetization were obtained, the magnetization was a linear function of H (Figs. 3 and 4). This means that condition (6) is fulfilled. Thus, at low temperatures, the magnetic behavior of the studied glasses depends strongly on the single ions, and, according to the behavior of $1/M$ at low temperatures, it is possible to judge about the relative quantity of the single ions. This is true if magnetization of single ions follows the Curie law.

In the model, described by Eq. (4), the Weiss constant, θ , of the clusters and the correlation between the single ions and the ions in the clusters can be determined from the experimental curves. For this aim, the function:

$$MT/H = A + BT/(T - \theta) \quad (7)$$

is convenient. The second term in Eqs. (4) and (7) does not describe the behavior of antiferromagnets at low temperatures. However, the average magnetization of the structurally disordered antiferromagnet changes slowly in this temperature range, approaching some finite quantity when $T \rightarrow 0$. Therefore, MT/H is approximately a linear function of T in the same region, and $MT/H \rightarrow A$ when $T \rightarrow 0$. Consequently, by extrapolating the experimental function MT/H to zero temperature, we find parameter A , as demonstrated in Fig. 7.

At high temperatures:

$$MT/H = A + B/(1 - \theta/T) \approx A + B(1 + \theta/T) \quad (8)$$

is a linear function of $1/T$ and approaches $(A + B)$ when $1/T \rightarrow 0$. By extrapolating the experimental function MT/H to zero value of $1/T$, we find $(A + B)$, as demonstrated in the inset of Fig. 7. In Table 3, we present the parameters A and B for various samples, together with the parameter $K = B/(A + B)$. According to Eq. (5) and taking into account that an effective magnetic moment at high temperatures is supposed to be identical both for separate ions and ions in clusters, the parameter K gives us the relative part of the ions in clusters. Now, when we know the parameters A and B , it is enough to substitute the experimental value of M (or MT) in Eq. (4) or in Eq. (7) at any $T > |\theta|$ in order to find the paramagnetic Neel temperature of the clusters (see θ_2 in Table 3). We have done this at three temperatures: 100, 150 and 300 K, and have taken the average values. Discrepancy between the results provides the experimental error margin. Such a procedure is valid only if the experimental dependencies follow the theoretical functions. The experimental function $MT(T)$ of the glass Dy5 deviates from the theoretical one at $T > 200$ K (see Fig. 7), and therefore we have used only the interval 100–200 K for this glass.

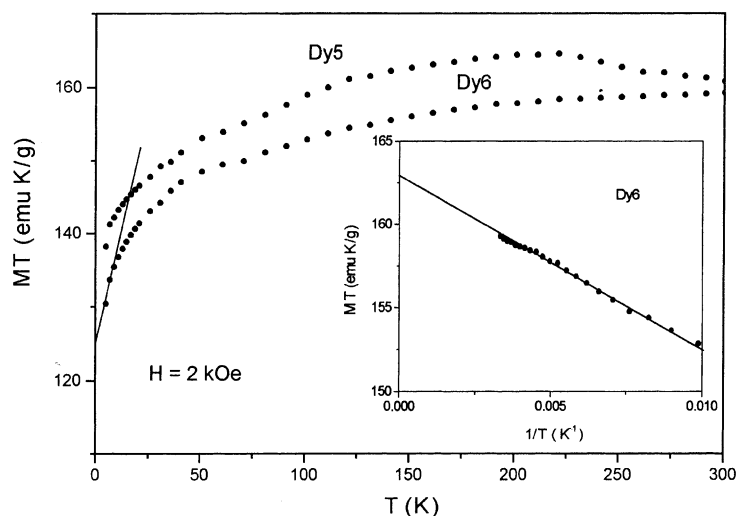


Fig. 7. Example of determination of parameters A and B from formula (4) by means of extrapolation of the product MT (see the text).

The parameter θ_1 , found by the linear extrapolation of the reciprocal magnetization, substantially differs from θ_2 , found by the above-described procedure, when parameter K is far from unity. In borate glasses with Dy [21], the paramagnetic Neel temperatures, derived by the linear extrapolation, were also small ($|\theta| \leq 6$ K). The reason for that can be the same as in the present study.

From Eq. (5) we have

$$A + B = m_{\text{eff}}^2(n_A + n_B)/3k = m_{\text{eff}}^2 n/3k, \quad (9)$$

where n is the total number of RE ions in 1 g of RE element. From Eq. (9) we calculate the effective magnetic moments of the RE ions in the glasses (see Table 3) with the help of parameters A and B found above. These are high temperature values of the effective magnetic moment. The magnetic moment of a free ion, $\mu_B g_J [J + (J + 1)]^{1/2}$, is equal to 10.64, 3.62, and 3.58 Bohr magnetons or according Van-Vleck theory: 10.6, 3.68 and 3.62 for Dy^{3+} , Nd^{3+} and Pr^{3+} , respectively [32]. In pure R_2O_3 oxides they are: 10.52 [33], 3.67 [34] and 3.59 [35] Bohr magnetons, respectively. It is seen that the experimental values of the effective magnetic moments in glasses are rather close to those of the free ions, however, they are appreciably smaller than are in corresponding RE oxides. This means that, in the high temperature region,

RE ions in the studied glasses are near to the free ones, but they are less free than in the pure oxides. Consequently, the RE ion environment in the glasses differs from that in the pure oxides. The appreciable decrease of m_{eff} with the increase of Dy concentration at the transition from Dy6 to Dy7 (Table 3) can testify to a change of the environment of Dy ions in the corresponding change of the Dy concentration. Some increase of the parameter K , describing correlation between two terms in (4), is also observed at the transition from Dy6 to Dy7 (Table 3).

The Curie–Weiss-type behavior of magnetic susceptibility can also be a consequence of the crystal field influence only [36]. The same is true for the behavior at $T < |\theta|$. Therefore, the sense of the first term in Eq. (4) and of the parameter A should be discussed in every specific case (see below).

In Table 3, the ratio $\chi(5)/\chi(300)$ of susceptibilities of the glasses at temperatures 5 and 300 K is given. If magnetization of the glasses followed the Curie law, the ratio would be equal to 60. It is seen that this ratio is less than 60 for all samples. Independent of the existence of the magnetic ordering, the lower the ratio the greater is the influence of the crystal field on the magnetic moment of the ion at low temperatures. Thus, the

influence of the crystal field decreases in the order: Pr, Nd, Dy glasses. This is naturally explained from the properties of ground states of the RE ions.

The ground states of Dy^{3+} , Nd^{3+} , and Pr^{3+} are ${}^6\text{H}_{15/2}$, ${}^4\text{I}_{9/2}$ and ${}^3\text{H}_4$, respectively. The ground states of Dy^{3+} and Nd^{3+} have a half-integer total moment J . Therefore, even in a low symmetry crystal field, energy levels remain doubly degenerated, i.e., they have effective spin of $\frac{1}{2}$. The levels, doubly degenerated due to half-integer total moment, have a magnetic moment without an external magnetic field, and this field only removes degeneration according to the projection of the magnetic moment on the field direction. The ground state of Pr^{3+} has the integer moment J . The crystal field of low symmetry, which is supposed to be the case in glasses, removes the degeneration of such states totally. The non-degenerated states obtained have no magnetic moment and acquire it only in a magnetic field, due to the mixing of the components of the crystal field splitting. Therefore, the magnetic susceptibility and the field of the magnetic saturation at low temperature are determined in this case not by the ratio of magnetic and thermal energies but by the ratio of magnetic field energy and the crystal field energy. All this means that, under other equal conditions, the influence of the crystal field in the case of Pr^{3+} should be larger than in the case of Dy^{3+} and Nd^{3+} . The shape of the magnetization curves at 5 K (Figs. 3 and 4), the same as the low field susceptibilities at low temperature, qualitatively agree with this conclusion, and they also provide the mentioned correlation between the influences of the crystal field on the different ions in definite environmental conditions.

Compounds of dysprosium frequently exhibit antiferromagnetic ordering. For example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$ [37], DyPO_4 [38], $\text{Dy}(\text{OH})_3$ [39] and DyOF [40] have zero-field ordering temperatures of 2.53, 3.39, 3.48 and 3.6 K, respectively. Paramagnetic Neel temperature of the oxide Dy_2O_3 was found to be -18 K [33]. Culea and Bratu [21] have determined the Weiss constants of some borate glasses containing Dy_2O_3 by linear extrapolation of the reciprocal susceptibility. At low concentrations of Dy_2O_3 paramagnetic Neel tem-

perature is equal to zero. This testifies to the existence of isolated Dy ions, which follow the Curie law. But beginning from some concentration of Dy_2O_3 , the Weiss constant is equal to ≈ -6 K, and this was attributed to the exchange coupled Dy ions [21]. The similar phenomenon was observed in glasses, containing Gd^{3+} ions [17,18]. This ion, the same as Dy^{3+} , has half-integer moment in the ground state. Thus, we can suppose that in our glasses an analogous situation takes place and that the procedure, described above, gives real paramagnetic Neel temperatures of some clusters and gives a correlation between numbers of the isolated ions and the ions in the clusters (parameter K). However, in Ref. [40] it is shown that theoretical temperature dependence of χ^{-1} of a single Dy^{3+} ion in the crystal field of C_{3v} symmetry in DyOF has the shape qualitatively similar to that observed in our glasses. At the same time, the theoretical Weiss constant is certainly smaller than the experimental one ($\theta = -9.2$ K) in the same DyOF crystal, which has $T_N = 3.6$ K. Thus, in any case, there are grounds to suppose that in the Dy glasses under discussion, there are isolated Dy^{3+} ions and ions in the clusters, whose magnetic behavior is influenced by the exchange interaction.

Temperature dependence of the magnetic susceptibility of Pr_2O_3 has been calculated theoretically by Kern [35], taking into account only the crystal field splitting of the ground state. Obtained dependence describes well his experiment and at high temperatures it obeys the Curie–Weiss law with $\theta = -72.9$ K. Measured magnetic moment of Pr_2O_3 at high temperature is 3.59 Bohr magnetons [35]. At low temperatures, both experimental and theoretical susceptibilities are almost constant, the same as in the case of magnetic ordering, but in contrast to the Pr containing glasses under consideration (Fig. 5). However, oxides, which deviate from the stoichiometric composition Pr_2O_3 , reveal the behavior of the susceptibility [35] similar to that of the studied glasses. Such behavior of the oxides was explained by existence of Pr^{4+} ions [35]. This ion has half-integer moment in the ground state and, consequently, it has higher susceptibility than Pr^{3+} in a crystal field at low temperature. At small deviation of Pr_2O_3 from the stoichiometry and in the studied glasses (Table 3),

magnetic moment and paramagnetic Neel temperature are smaller than those in the pure oxide (for $\text{PrO}_{1.72}$: $m_{\text{eff}} = 2.82$ Bohr magnetons and $\theta = -36$ K [35]). Thus, the behavior of the magnetic susceptibility in the Pr containing glasses at low temperatures can be considered as a consequence of existence of Pr^{4+} ions and parameter A in Eq. (4) characterize the contribution of these ions into the susceptibility of the glasses. Indeed, the larger the parameter A the smaller is $|\theta|$, the smaller is the high temperature m_{eff} and the larger is the low temperature susceptibility (Table 3).

Temperature dependence of the reciprocal magnetic susceptibility of the shape observed for the Nd glass (Fig. 5) can be obtained, taking into account only the crystal field splitting of the ground state [41]. Paramagnetic Neel temperature of Nd_2O_3 is -27 K [32]. This is rather close to θ_1 of the Nd glass found directly by extrapolation of the high temperature part of the reciprocal susceptibility. Thus, the parameters $A(B)$ and θ_2 in this case are the formal ones which only permit us to describe the experimental dependence by formula (4), but have no physical sense. However, the possibility of describing the temperature dependence of the magnetic susceptibility of some RE compounds with the help of crystal field influence only does not exclude the existence of the magnetic ordering [42].

It is known that at $T = T_N$ the magnetic susceptibility of antiferromagnets exhibits a change in the slope. Such a break in the data may help in identifying the T_N of the clusters. For the convenience of observation of small features, we have depicted in Fig. 8 the difference between the experimental function $M(T)$ and the first term in Eq. (4), with the determined values of parameter A for some glasses. Corresponding curves for all glasses exhibit a change in the slope in the region of $T = 7$ K. This can testify to an antiferromagnetic ordering and, consequently to a clustering.

The magnetic susceptibility is proportional to m_{eff}^2 . The maximum susceptibilities of Dy, Pr and Nd glasses at room temperature are then brought approximately into the correlation 8.7:1:1, respectively. Magneto-optical activities, C_0 , of the same

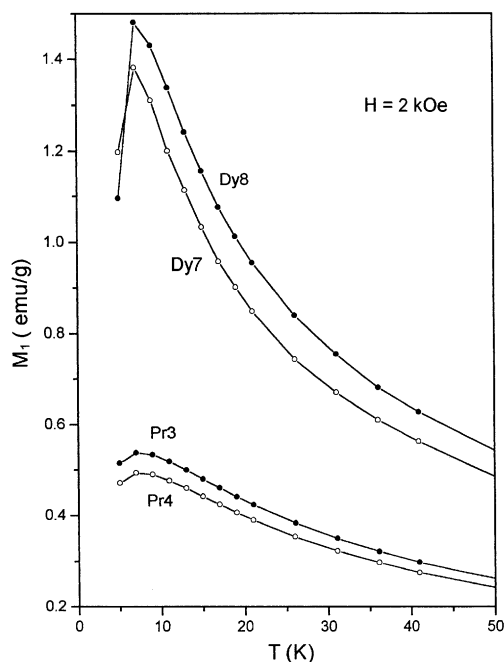


Fig. 8. Magnetization $M_1 = M - AH/T$ per gram of RE atoms (see the text).

glasses (Table 2) are approximately brought into the correlation 3.4:3.4:1 for the largest values and 2.6:1.6:1 for the smallest values. According to Eq. (3): $\chi \sim C_0 g$. Lande factors, g , of Dy^{3+} , Pr^{3+} , and Nd^{3+} are $\frac{4}{3}$, $\frac{4}{5}$, and $\frac{8}{11}$, respectively. The values $C_0 g$ are then brought into the correlation 6.2:3.7:1 for the largest values and 4.7:1.8:1 for the smallest values, which also disagrees with the correlation of the susceptibilities. There is no definite correlation between m_{eff} and C_0 for the different glasses with the same RE ion as well (compare Tables 2 and 3). Thus, the magneto-optical activity is indeed not strictly proportional to the magnetic susceptibility, when we compare different materials with the different paramagnetic ions.

4. Summary and conclusion

Magneto-optical FR in a number of oxide glasses containing Pr^{3+} , Dy^{3+} , and Nd^{3+} ions was measured as a function of light wavelength (240–1000 nm) and temperature (80–350 K).

Magnetization of the same glasses was measured as a function of magnetic field (0–50 kOe) and temperature (5–300 K). Dispersion of the FR has permitted us to find the positions of the effective transitions responsible for the FR, as well as their magneto-optical activities. Magneto-optical activity weakly depends on the concentration of the RE ion (in the same matrix), appreciably depends on the matrix (with the same RE ion), and strongly depends on the type of RE ion.

Temperature dependencies of the FR in the studied glasses follow the Curie–Weiss law rather well. Small deviations from this law in some glasses can be attributed to the influence of the temperature independent FR. Temperature dependencies of the FR are approximately proportional to those of magnetic susceptibility. However, the magneto-optical activity is not proportional to the magnetic susceptibility, when we compare different materials with the different paramagnetic ions.

Temperature dependencies of magnetic susceptibility of all glasses (with the exception of Dy³⁺) strictly follow the Curie–Weiss law in the high temperature region. This means that the temperature independent susceptibility is negligibly small in the studied temperature range within the limit of the experimental error. Weiss constants of all glasses are negative. High temperature magnetic moments of RE ions in the glasses are rather close to those of the free ions; however, they are smaller than in the corresponding RE oxides.

At low temperatures all studied glasses reveal downward curvature of the reciprocal magnetization variation with decreasing temperature. For Nd glass such behavior can be qualitatively accounted for by the influence of crystal field only. For Pr and Dy glasses this is not enough. Such behavior can be described also by introducing the term proportional to $1/T$ into the susceptibility. It was shown that in Pr glasses this term can characterize the contribution of the Pr⁴⁺ ions. For Dy glasses, the grounds have been offered for the conclusion that there are antiferromagnetically ordered clusters and isolated atoms in these glasses.

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