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State of Atoms and Interatomic Interactions in Perovskite-Like Oxides: XXXIV.[1] State of Europium Atoms and Exchange Interactions in $La_{1-y}Eu_yAlO_3$

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Abstract—A series of solid solutions of the $La_{1-y}Eu_yAlO_3$ composition was studied by the method of magnetic dilution in the concentration range 1–20 mol % of europium atoms. Europium atoms in the solid solutions were found to take part in the antiferromagnetic superexchange interactions. Magnetic characteristics at the infinite dilution are described as existence of single Eu(III) atoms with a large contribution of Van Vleck's temperature independent paramagnetism (~0.001 emu/mol).

Keywords: magnetoresistivity, lanthanum manganites, perovskite structure, magnetic susceptibility, ceramic procedure of synthesis

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In recent years increasing attention of researchers is paid to the studies of magnetic and electrical characteristics of complex oxides with perovskite structure containing various doping elements [2-4]. This interest is defined first of all by the effect of colossal magnetoresistance found in lanthanum manganites containing alkaline earth elements, $La_{1-x}A_xMnO_3$ (A = Ca, Sr) [5, 6]. At present an active search for the compositions with optimal functional properties for the use in technology is going on. The magnetoresistance is known to be influenced not only by the nature of alkaline earth elements, but also by introducing *f*-elements into the perovskite structure. In the recent years the introduction of europium atoms was shown [7–9] to improve the magnetoresistive properties of lanthanum manganites in comparison to the use of other rare earth elements. However, the absence of a unique model allowing the properties of functional ceramics to be related to the diamagnetic composition results in the fact that the search for doping elements is carried out empirically. The method of magnetic dilution based on the study of magnetic properties of the solid solutions of isomorphous substitution allows the influence of doping elements on magnetic characteristics of the materials to be traced.

In the present work the state of europium atoms and exchange interactions in the $La_{1-y}Eu_yAlO_3$ solid solutions were studied with the help of magnetic dilution method. With this aim in view a series of $La_{1-y}Eu_yAlO_3$ solid solutions (y = 0.02, 0.05, 0.10, 0.15, 0.20) was prepared by the ceramic procedure.

Parameters of rhombohedral (trigonal) unit cells were calculated for the obtained solid solutions from the X-ray analysis data (Table 1). The trigonal crystal system is caused by the distortion of the cubic structure. The dependence of unit cell parameters on europium content in the samples shows that the unit cell parameter (a) and the unit cell volume decrease as europium atoms are added. The linearity of the dependence of unit cell parameters on the content of europium atoms in the samples shows that no phase transitions occurs when the europium content in solid solutions increases in the concentration range under study.

The paramagnetic components of magnetic susceptibility reduced to 1 mole of europium atoms and effective magnetic moments were calculated from experimental specific magnetic susceptibilities.

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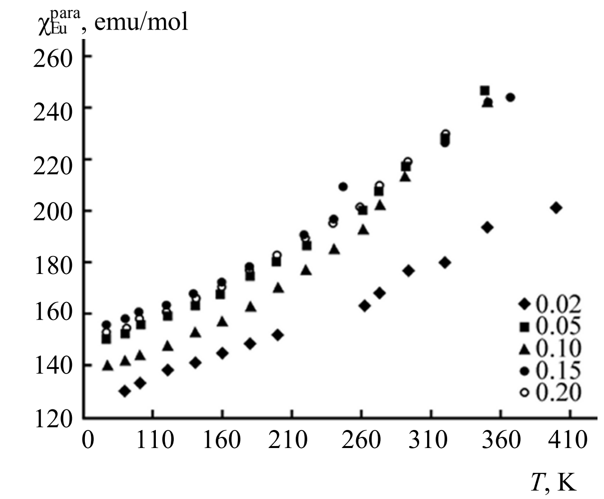

Fig. 1. Plot of inverse magnetic susceptibility, $1/\chi_{Eu}^{para}$, vs. temperature for the $La_{1-y}Eu_yAlO_3$ solid solutions.

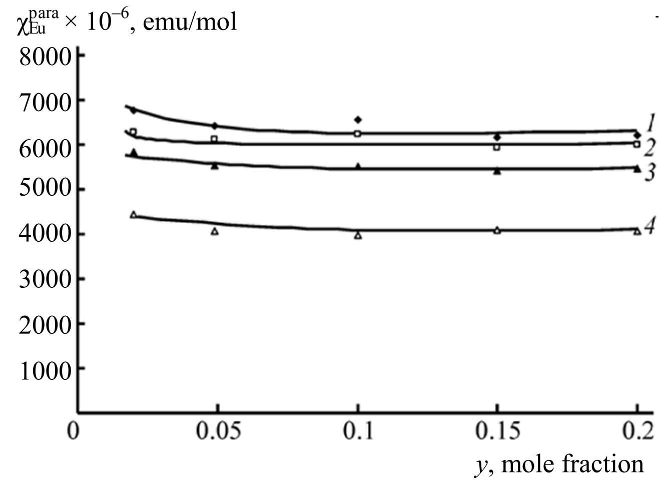

Fig. 2. Plots of paramagnetic components of magnetic susceptibility calculated per 1 mole of europium atoms, χ_{Eu}^{para}, vs. mole fractions of europium atoms in the $La_{1-y}Eu_yAlO_3$ solid solutions for (*1*) 120, (*2*) 160, (*3*) 220, and (*4*) 400 K.

Temperature dependences of the inverse paramagnetic component of magnetic susceptibility (χ_{Eu}^{para}) are given in Fig. 1. For all solid solutions the Curie-Weiss law is not obeyed. According to [10], when calculating magnetic characteristics of the systems containing europium atoms, it is necessary to take into account the occupation of not only the nearest F_1 term, but also of the next three excited states. These factors may result in the deviations from the Curie-Weiss law.

The effect of magnetic dilution is clearly observed in the magnetic susceptibility isotherms reduced to one mole of europium atoms (Fig. 2), χ_{Eu}^{para} slightly decreases as the concentration of europium atoms in the system increases. Such a run of magnetic susceptibility isotherms points to the fact that in the concentration range under study europium atoms do interact between each other, this interactions being antiferromagnetic.

Table 1. Unit cell parameters for the $La_{1-y}Eu_yAlO_3$ system

y	*a*, Å	α, deg	*V*, Å^3
0.02	5.3570(16)	60.100(62)	109.23(26)
0.049	5.3556(17)	60.101(65)	108.87(26)
0.10	5.3523(16)	60.111(62)	108.69(25)
0.15	5.3498(14)	60.114(63)	108.797(26)
0.203	5.3469(15)	60.119(58)	108.38(23)

The values of effective magnetic moments at the infinite dilution ($\mu_{eff}^{x\to 0}$) were obtained by extrapolating the isotherms of paramagnetic component of magnetic susceptibility and the effective magnetic moments to the infinite dilution ($x\to 0$). They are given in Table 2.

The found values of effective magnetic moments at $x\to 0$ point to the existence of single europium atoms at the infinite dilution, the experimental value of μ_{eff} for them being 3.4 BM at room temperature. The temperature dependences of the effective magnetic moments at the infinite dilution ($\mu_{eff}^{x\to 0}$) for the $La_{1-y}Eu_yAlO_3$ solid solutions under study and for single Eu(III) atoms in the complex compound $Eu_2(C_2O_4)_3\cdot 10H_2O$ are given in Fig. 3. The effective magnetic moment for this compound was calculated by the quantum chemical method and was confirmed experimentally [10]. The effective magnetic moment $\mu_{eff}^{x\to 0}$ in the solid solutions under study increases as the temperature increases and tends to zero at 0 K for the F_0 ground term.

The ground state of Eu(III) atoms is characterized by $L = 3$, $S = 6/2$, $J = 0$, $g = 0$, term $^7F_0$. According to *j–j* interaction model, the effective magnetic moment of europium atoms must be equal to zero. According to the published data [10] the experimental effective magnetic moment of Eu(III) is ~3.4 BM at room temperature. A discrepancy between theoretical and experimental values of the effective magnetic moment is accounted for by a small difference in levels of the lowest and the first excited states, which results in the temperature occupation of the nearest excited states. In this case the magnetic susceptibility of europium compounds must be the sum of the temperature dependent part and the Van-Vleck's paramagnetism contribution (temperature independent paramagnetism).

$$\chi_{para} = \frac{N\mu^2\beta^2}{3kT} + 2N\alpha.$$

Here N is the Avogadro number, T is temperature, N_α is Van-Vleck's paramagnetism, μ is the magnetic moment, and β is Bohr magneton.

Paramagnetic component of magnetic susceptibility for the $La_{1-y}Eu_yAlO_3$ solid solutions under study at $x\to0$ is described by the following formula:

$$\chi_{tot} = \frac{N\mu^2\beta^2}{3kT} + 0.001.$$

Here 0.001 emu/mol is the Van-Vleck's paramagnetism. Such a high value of Van-Vleck's paramagnetism is not encountered in *d*-elements, however in the compounds of *f*-elements the values of Van-Vleck's paramagnetism may be as much as 10^{-2} emu/mol [11].

The electron paramagnetic resonance spectrum for the $La_{0.98}Eu_{0.02}AlO_3$ solid solution is given in Fig. 4. In the ESR spectrum of the studied sample there is a signal typical of bivalent europium atoms. The total moment of trivalent europium Eu(III) is equal to zero, i.e. the signal from these ions will be absent from the ESR spectra. The detection of Eu(II) in the ESR spectra points to the fact that even in the absence of the stoichiometric possibility for the reduction of Eu(III) to Eu(II) there is a small (less than 0.001%) admixture of this state, may be due to a weak oxygen non-stoichiometry, which does not affect the magnetic susceptibility, but points to the fact that europium can be easily reduced.

Table 2. Effective magnetic moments ($\mu_{eff}^{x\to0}$) and paramagnetic components of magnetic susceptibility ($\chi_{Eu}^{para,x\to0}$) at the infinite dilution for $La_{1-y}Eu_yAlO_3$

T, K	$\mu^{x\to0}$, BM	$\chi_{Eu}^{para,x\to0} \times 10^{-6}$, emu/mol
90	2.29	7220
100	2.39	7080
120	2.6	6980
140	2.83	7090
160	2.95	6740
180	3.12	6710
200	3.24	6510
220	3.32	6210
240	3.42	6040
260	3.54	5980
273	3.59	5850
293	3.67	5700
320	3.73	5390
350	3.83	5200
400	3.81	4500

Therefore the results of measuring the magnetic susceptibility and the examination of the obtained magnetic characteristics show that europium atoms in

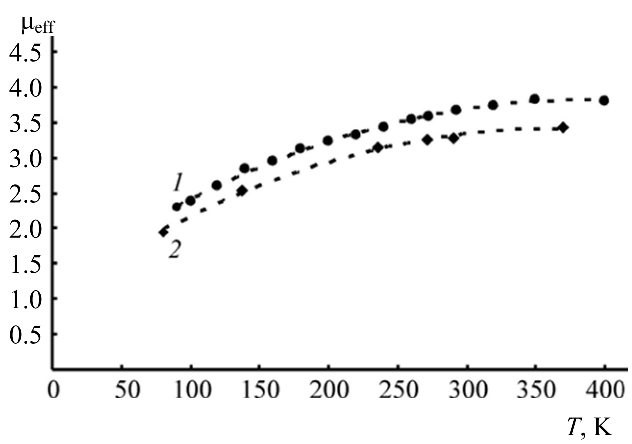

Fig. 3. Plots of (*1*) experimental and (*2*) theoretical effective magnetic moments at infinite dilution ($\mu_{eff}^{x\to0}$) vs. temperature.

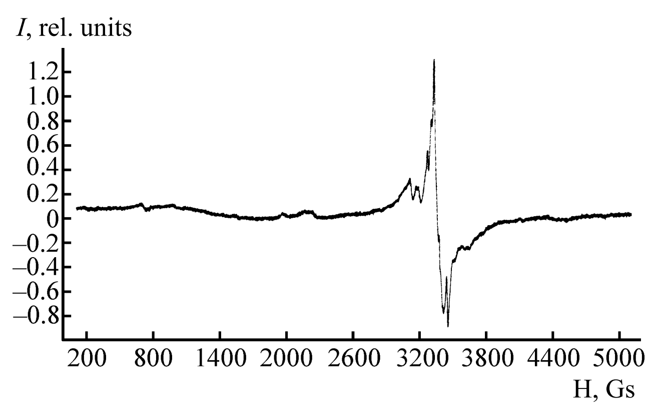

Fig. 4. EPR spectrum for $La_{0.98}Eu_{0.02}AlO_3$.

the $La_{1-y}Eu_yAlO_3$ solid solutions take part in the superexchange interactions of the antiferromagnetic type. The magnetic characteristics at the infinite dilution are described in the context of single Eu(III) atoms with a substantial contribution of the Van-Vleck's temperature-independent paramagnetism (~0.001 emu/mol) and the temperature-dependent effective magnetic moment.

EXPERIMENTAL

A series of $La_{1-y}Eu_yAlO_3$ solid solutions was obtained by ceramic procedure. We used for the synthesis the following reagents: specially pure grade lanthanum and europium oxides and aluminum γ-oxide prepared in laboratory conditions. Stoichiometric amounts of initial substances calculated by the equation of solid phase reaction (1) were homogenized for 1h in a jasper mortar, pelleted, and sintered at 1450°C for 23 h with slow increase in temperature till single phase samples were obtained with the magnetic susceptibility independent of the further sintering time.

$$(1-y)La_2O_3 + yEu_2O_3 + Al_2O_3 = 2La_{1-y}Eu_yAlO_3. \quad (1)$$

The content of europium atoms in the solid solutions was determined by the method of atomic emission spectroscopy with inductively bound plasma (ICP-AES Optima 7000 DV, Perkin Elmer, USA). The error did not exceed 5%.

The single-phase state of the samples was confirmed by the X-ray diffraction analysis. The powder X-ray patterns were recorded on DRON-3 and Rigaku MINIFLEX X-ray powder diffractometers using CuK_α emission. The unit cell parameters were calculated using the PDWin program package. The X-ray patterns were recorded in the Service center "Roentgen diffraction investigation methods" of St. Petersburg State University. The electron spin resonance spectra were recorded on a Bruker Elexsys E580 spectrometer in "Research Resources Center for Magnetic Resonance" of St. Petersburg State University.

We measured the magnetic susceptibility by the Faraday method in the temperature range 77–400 K.

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