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Magnetic susceptibility and parameters of electronic structure of Al_2R (R = La, Ce, Sm, Gd, Dy, Ho, Yb) intermetallic compounds at high temperatures.

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Abstract. Magnetic properties of intermetallic compounds Al_2R (R = La, Ce, Sm, Gd, Dy, Ho, Yb) are investigated in a wide temperature (20-1650^0 C) and magnetic fields (0,3-1,3 T) ranges. For all the samples the increase of magnetic susceptibility with temperature growth was found in liquid state. From experimental data several parameters of electronic structure of the compounds were obtained. In particular, it was shown that the values of effective magnetic moment per rare earth atom in compounds are lower than for ion R^{3+}.

1 Introduction

According to contemporary views, the main cluster forming element for Al-REM melts is the so-called "quasimolecules" Al_2REM [1-4]. These associates have a tendency to polymerization, i.e. to formation of global nets and chains that provide high glass forming ability of the melt. Our previous experimental and theoretical investigations showed that in liquid dilute Al-REM alloys and first intermetallic compounds $Al_{11}REM_3$ or Al_3REM, associates Al_2REM exist even at high overheating above liquidus [1, 4]. From thermodynamics modeling results it comes that they can exist in melts even at temperatures higher than 2000 K [5].

For dilute Al-REM alloys and first intermetallic compounds an important fact was discovered - the value of effective magnetic moment per rare earth atom is substantially lower than for the free ion R^{3+} [1,3,4]. The idea was suggested that in alloys and compounds with aluminum REM atoms exist not in trivalent ion form, but create chemical bonds of covalent – metallic type with the participation of 4f-electrons.The involvement of 4f-electrons into chemical bonds formation affects significantly the effective magnetic moment per REM atom. The decay of Al_2REM associates, i.e. the destruction of the directed bonds, begins above the melting temperature of Al_2REM compounds; 4f-electrons are localizing on atoms, changing the magnetic moment per REM atom significantly, which in turn affect the total magnetic susceptibility of an alloy - a sharp increase in χ values takes place.

However, it is a common place in many works that in alloys and compounds with non-transition metals, aluminum, in particular, REM do not form chemical bonds with f-electrons and exist in a state of trivalent ions, see for example [8-12].

Thus, the study of magnetic properties and electronic structure of Al_2REM compounds themselves in a wide temperature range, including solid and liquid states, becomes an actual problem. At the same time, the available data on these intermetallics are limited and focused mainly on low-temperature studies [9,10,12]; the results obtained for temperatures above 300 K, and especially in the liquid state, are very scanty and contradictory [11].

2 Experiment

2.1 Method

Magnetic susceptibility studies were performed by Faraday's method on a setup described in details in [6]. The temperature range was t = 20-1700^0 C, an applied magnetic field - B = 0,3-1,3 T. All the experiments were carried out in crucibles of beryllium oxide. The chamber was pre-evacuated to a residual pressure of 10^{-2} Pa and then filled in with high-purity helium A (99,995 vol.%) to a pressure of $1.2 \cdot 10^5$ Pa. Susceptibility temperature curves χ (T) were obtained during heating and subsequent cooling with the step 10-15^0 and isothermal expositions for 3-5 minutes. at each temperature. The uncertainty in susceptibility absolute values definition did not exceed ± 2%.

2.2 Preparation and analysis of compounds

Polycrystalline samples were obtained from pure aluminum (99.999 %) and rare earth metals (lanthanum, cerium, samarium, gadolinium, dysprosium, holmium, ytterbium of 99.86 % purity) by triple arc-melting in an argon atmosphere. The chemical composition of the samples was checked by atomic emission analyzer Spectrum Flame Modula S. Phase composition and lattice parameters of intermetallic compounds were determined by X-ray analysis. Almost all compounds have stoichiometric composition Al_2R and were single phase. The experimental values of unit cell parameters a_{exp} together with literary data - a_{ref}, [7] are given in Table 1.

Table 1. The unit cell parameters for intermetallic compounds Al_2R

№	A_2R	a_{exp}, Å	a_{ref}, Å[7]
1	A_2La	a=8,145	a=8,148
2	A_2Ce	a=8,071	a=8,064
3	A_2Sm	a=7,940	a=7,940
4	A_2Gd	a=7.889	a=7,899
5	A_2Dy	a=7,828	a=7,829
6	A_2Ho	a=7,812	a=7,813
7	A_2Yb	a=7,867	a=7,881

3 Results

The temperature dependences of magnetic susceptibility in investigated intermetallic compounds are presented at figures 1 – 4.

For Al_2Dy, Al_2Ho and Al_2Gd magnetic susceptibility decreases following Curie - Weiss law in the range 20 ^{0} C – t_M. In liquid state an increase of susceptibility with temperature growth was found out for these compounds (figure 1).

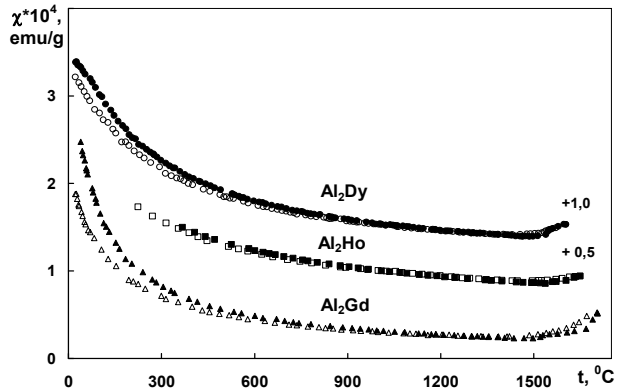

Fig. 1. Magnetic susceptibility vs temperature for Al_2Dy, Al_2Ho and Al_2Gd intermetallic compounds (●, ■, ▲ - heating; ○, □, Δ – cooling; +0,5; +1,0 – shift of curves in ordinate axis)

A similar temperature dependence χ(T) was obtained for intermetallic Al_2Ce (figure 2): susceptibility decreases following Curie - Weiss law in the range 20 -800^0 C, remains practically constant in the range 800-1480 ^{0} C and sharply increases above melting.

For Al_2Ce compound the time dependence of susceptibility was studied at t = 1500^0 C and t = 1550^0 C for 90 min and 120 min respectively. Magnetic susceptibility was found to be independent on time within mentioned error bars (± 2 %).

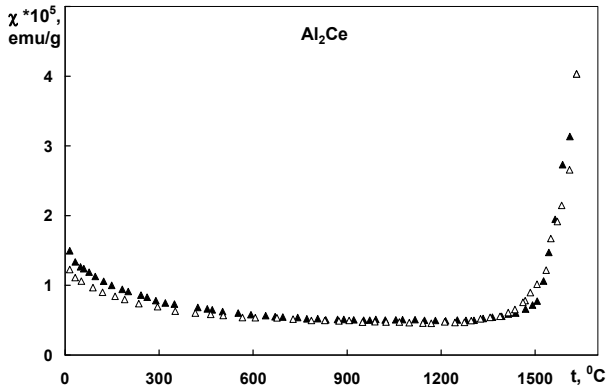

Fig. 2. Magnetic susceptibility vs temperature for Al_2Ce intermetallic compound (▲-heating; Δ - cooling).

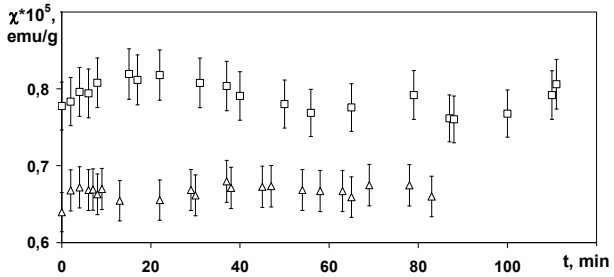

Fig. 3. Magnetic susceptibility vs time for Al_2Ce intermetallic compound at t_1 = 1500^0 C (Δ) and t_2 = 1550^0 C temperatures (□), (accuracy on figure - ±2 %)

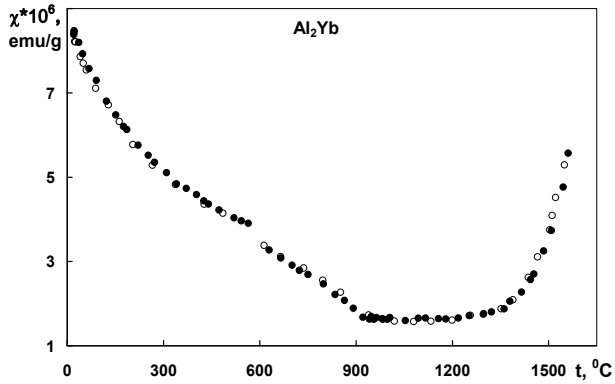

Fig. 4. Magnetic susceptibility vs temperature for Al_2Yb intermetallic compound (● - heating; ○ - cooling).

As for Al_2Yb, the experiment revealed a more complex temperature dependence of χ(T). It follows Curie-Weiss law from room temperature to t = 900^0 C only, at which a distinct kink in temperature curve is recorded. In the range 900-1360^0 C, the values of χ are

practically unchanged. Above the temperature t = 1360^0 C, which corresponds to the melting point of intermetallic compound Al_2Yb, an increase of magnetic susceptibility is fixed (figure 4).

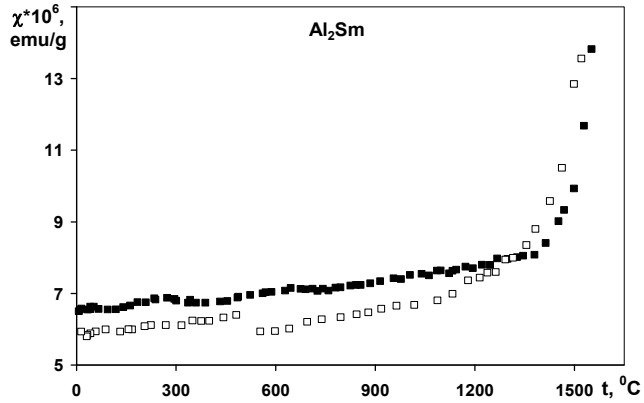

Fig. 5. Magnetic susceptibility vs temperature for Al_2Sm intermetallic compound (■ – heating; □ - cooling).

The unusual behavior of magnetic susceptibility is discovered for the intermetallic compound Al_2Sm - χ increases within entire temperature range (figure 5). In crystalline state, the susceptibility linearly grows up with temperature. Above the melting point (t = 1480^0 C) the sudden change of temperature coefficient and a significant, nonlinear increase of susceptibility is revealed. The noncoincidence of heating and cooling curves (hysteresis of property) in solid state below t = 1200^0 C is discovered for this sample. We connect this fact with high aggressiveness of the material (Al_2Sm) in liquid state to the material of crucible mainly, as well as with oxidation of the sample.

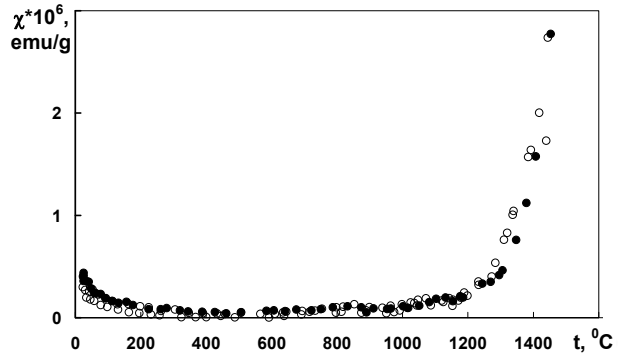

Fig. 6. Magnetic susceptibility vs temperature for Al_2La intermetallic compound (● - heating; ○ - cooling).

The experiment with Al_2La compound showed that this material has a very low absolute χ values (figure 6). In the range t = 20-600^0 C susceptibility varies from 4 *10^{-7} to 0,8 * 10^{-7} emu/g. and can be fitted by a generalized Curie-Weiss law. Above t = 600^0 C and up to the melting point susceptibility values vary slightly, while the temperature coefficient has a positive value. The significant growth of susceptibility is recorder in liquid state.

4 Discussion

For all the compounds (except for Al_2Sm) magnetic susceptibility temperature curves in solid state were approximated by the generalized Curie - Weiss law:

$$\chi_p(T) = \chi_0 + \frac{C}{T-\Theta}, \quad (1)$$

where C - Curie constant, Θ - paramagnetic Curie temperature, χ_0 - temperature-independent contribution to the magnetic susceptibility, defined by the density of electronic states near Fermi level $N(E_F)$ only. The latest was determined from the equation describing Pauli paramagnetism of conductive electrons:

$$\chi_0 \cong 2N_A M^{-1}\mu_B N(E_F)\xi\ , \quad (2)$$

here N_A - Avogadro's constant, M - molar mass, ξ - a factor of exchange amplification (for rare earth metals ξ = 1.5, as a rule [8]).

Because aluminum is a weak magnetic material, the effective magnetic moment was calculated per rare earth atom only:

$$\mu_{eff} = \sqrt{\frac{3kCM}{\alpha N_A(\mu_B)^2}}, \quad (3)$$

where k - Boltzmann constant, μ_B - Bohr magneton, α - atomic fraction of rare-earth metal in the compound.

The results of calculations of electronic properties (electronic density of states near Fermi level - N (E_F), effective magnetic moment per REM atom - μ_{eff}, paramagnetic Curie temperature - Θ) for investigated intermetallic compounds are presented in Table 2. The known literature data for the effective magnetic moments in intermetallic compounds Al_2R and in pure rare earth metals are given in this table as well.

From Table 2 one can see that the temperature-independent term χ_0 has small value in comparison with the total susceptibility (lower for 10 and more times). This indicates an insignificant contribution of conductive electrons into magnetic susceptibility of the compounds.

The density of electron states near Fermi level N (E_F) non-monotonically increases from 0,02 eV^{-1} for Al_2La up to 7,7 eV^{-1} for Al_2Ho and decreases to 2.6 eV^{-1} for Al_2Yb.

The value of paramagnetic Curie temperature depends on interaction of magnetic moments with each other and with intercrystalline field: the more the interaction – the more θ. However, we obtained rather complicated behavior of θ with maximum for Al_2Gd and minimum for Al_2Ce (see table 2). Let us mention, that paramagnetic temperature values are in good correlation with Curie or Neel temperatures for these compounds. For example, T_N = 2 K for Al_2Ce; T_C = 170 K for Al_2Gd; T_C = 58 K for Al_2Dy etc [10].

For the studied intermetallic compounds effective magnetic moment per REM atom was found to be lower than for the ion R^{3+}. It means that in these compounds rare earth atoms exist not in form R^{3+}, as it was previously thought [8, 9, 11], but create some directed

bonds of covalent type with aluminum atoms. The situation is similar to described in [1, 4]. 4f-electrons are involved into bonds formation and that is why their partial delocalization from REM atoms takes place.

Table 2. Parameters of electronic structure for Al_2R compounds in solid state

Al_2R	Al_2La	Al_2Ce	Al_2Gd	Al_2Dy	Al_2Ho	Al_2Yb
$\chi_0 \cdot 10^6$, emu/g	0,014	2,1	3,75	4,82	5,1	1,7
$C \cdot 10^3$, emu·K/g	0,099	3,06	30,6	54,6	56	2,8
θ, K	57	5,3	187,3	73,1	44,7	11
N(EF), eV^{-1}	0,02	2,79	5,4	7,14	7,7	2,6
μ_{eff}, μ_B	0,39	2,17	7,2	9,7	9,9	3,7
μ_{eff}, μ_B literature data		2,54 [9]	7,92 [10]	9,7 [10] 10,98 [11]	10,8 [11]	
θ, K literature data		-33+9 [9]	180 [10]	68 [10] 33 [11]	35 [8]	
μ_{eff}, μ_B for pure REM	0,49 [10]	2,51 [9]	7,98[9] 8,07 [13]	10,65 [12] 10,67 [13]	11,2 [12], 10,8 [13]	4,5 [12]

On melting of Al_2R intermetallics, 4f-electrons begin to localize on REM atoms again. This leads to an increase in magnetic moment, and, consequently, in total magnetic susceptibility, as one can see from the experimental data. The idea about covalent bonds between aluminum and rare earth atoms was confirmed in [14] also.

5 Conclusions

Experimental studies of magnetic susceptibility (by Faraday's method) in intermetallic compounds Al_2R (R = La, Ce, Sm, Gd, Dy, Ho, Yb) in a wide range of temperature, including solid and liquid states, are performed. The experimental curves are fitted by a generalized Curie-Weiss law and some parameters of electronic structure are obtained. The results are discussed in the assumption of the existence of directed bonds between rare earth atoms and aluminum atoms. A part of 4f-electrons is involved into formation of these bonds and that is why electronic parameters (the small values of effective magnetic moment per REM atoms, in particular) of compounds differ from those for pure REM.

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