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The role of rare-earth atomic collapse in the formation of Al-rich metallic glasses

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Abstract. The role of rare-earth atomic 'collapse' in the formation and thermodynamics of aluminium-rich metallic glasses is studied, using the example of the $Al_{90}La_{10}$ metallic glass. Monte Carlo simulations are carried out for structural models containing 500 atoms in a cubic cell with periodic boundary conditions. The change of the pair interaction due to the atomic collapse is taken into account. An equivalent Ising Hamiltonian, accounting for the collapse transitions, is introduced. The Ising Hamiltonian is used to calculate the temperature dependence of the specific heat, which exhibits two temperature humps associated with the decollapse of the La atoms. The corresponding temperature is close to the experimentally measured temperature at which crystallization of the glass begins.

1. Introduction

A group of Al-rich metallic glasses has recently attracted attention. Their typical content is close to $Al_{90}RE_{10}$ where RE denotes a rare-earth element. They are usually ductile, and have tremendous strength and high corrosion resistance which seem to be connected with a high local stability of the corresponding compositions [2, 3]. One of the important issues in the formation of such metallic glasses is the fact that the RE-to-Al ratio of about 1:9 violates the standard atomic size criterion for glass formability [4].

We reported in our previous paper [1] the anomalous approach of atoms in $Al_{90}La_{10}$ metallic glasses. Our simulations show that the La atoms are always well separated from each other by Al atoms and that nearly every La atom has an Al neighbour at a distance smaller than the sum of their characteristic atomic radii. This feature can be observed in the radial distribution function as a small prepeak in front of the main peak of the distribution. It is worthwhile mentioning that the possibility of shortening of interatomic distances was discussed by Turnbull [5] for several transition-metal-based glasses.

One may argue that this anomalous approach creates an excessive pressure on the La atoms which can, in principle, cause charge-transfer processes and, hence, a change of the electronic configuration of the rare-earth atoms. This, in turn, may have an impact on the properties of the glass. The purpose of the present paper is to study the role played by these charge-transfer processes, via the so-called atomic collapse phenomena.

Mayer was concerned in [6] with the peculiarities of rare-earth atoms, which primarily consist of a sudden increase of the 4f-electron binding energy and a contraction to smaller radii ('collapse') of the 4f-electron orbit as the atomic number Z increases. Band and Fomichev [7] found, by means of Dirac–Fock calculation, a possibility of coexistence of two different states

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with the same configuration of the lanthanum and other atoms. The atoms in these states have different energies. A 4f electron in the first, collapsed, state moves into an inner well of its effective potential while in the second, blown, state it moves into an outer well.

The total atomic energy in the collapsed state is 2 to 3 eV higher than in the blown state. The change in atomic size for different rare-earth elements may be about 20% [8]. Considering both the anomalous approach and the possible collapse of the rare-earth atoms, one may expect this to open a way to an additional relaxation of the system and that it may have an important impact on the thermodynamics. The transfer to the collapsed state, which costs some energy, is accompanied by a decrease of the rare-earth-atom radius. Such a change of the rare-earth-atom radius can cause a decrease of the structural part of the glass energy. That is why we find it interesting to address the question of the collapsed–blown-state transitions in the Al-rich glasses.

A simulation of the same system, $Al_{90}La_{10}$, as in reference [1] is carried out, allowing for the possibility of the blown–collapsed-state transitions. The next section will outline the model potential and some details of the techniques used in the simulation. The results will be described and discussed in the third section. The principal aim of our investigation is to determine the role of the rare-earth atomic collapse in the formation and thermodynamics of this class of metallic glasses. To address these issues, we propose to consider an equivalent Ising model in which the blown–collapsed-state transitions are described by spin flips.

2. The model potential and simulation procedure

First, we address the problem of how to construct a potential which describes the interaction between Al–La pairs in both 'blown' and 'collapsed' states of La. The pair potential $U_{\mathrm{La-Al}}$ is the only one in which the collapse may be of importance. La atoms are well separated from each other and changes in their atomic structure do not influence the interaction in La–La pairs. As for Al–Al pairs, there is no place for collapse here at all.

The new potential corresponding to the collapsed state of the atom should take into account the fact that the trivalent La atoms convert into divalent ones with a smaller atomic radius and larger energy of the electron shell. In fact, we will consider a situation in which the rare-earth atoms have an additional degree of freedom associated with the possibility of a transition to the collapsed state. The shape of the pair potential changes due to this transition.

The Lennard-Jones potential

$$U_{\alpha-\beta} = B_{\alpha-\beta} r^{-12} - A_{\alpha-\beta} r^{-6} \tag{1}$$

for the interaction between the atom α and the atom β is usually quite sufficient for a simulation of the principal thermodynamic properties of the glass. Such a potential allows for good agreements with the experiment for most other systems [9]. Here the parameter $A_{\alpha-\beta}$ describes the dipole–dipole interaction between pairs of atoms and depends on the radii and numbers of the valence electrons of the interacting atoms. These parameters for the Al–Al, La–La, Al–La, Al–$\mathrm{La^{coll}}$ pairs are calculated with the known La radii for the blown (1.87 Å) and collapsed (1.63 Å) states, with the Al radius being 1.43 Å. (The superscript 'coll' denotes the collapsed state of the atom.) The parameters $B_{\mathrm{Al-Al}}$ and $B_{\mathrm{La-La}}$ are chosen from Monte Carlo simulations for pure Al and La, such that the first peaks of the radial distribution functions and the densities correspond to their respective values in the crystalline phases.

In order to determine the values of the parameter B_{La} for the blown and collapsed states, we use the radial distribution function obtained by XAFS for $Al_{91}La_9$ metallic glasses [10]. The parameters B_{La} and $B_{\mathrm{La^{coll}}}$ are initially chosen in such a way that the minima of the two pair potentials are at 3.3 Å and 2.9 Å for the blown and collapsed states respectively. After the

simulations were done, these B-values were corrected in order to achieve a better agreement between the experimental and theoretical radial distribution functions. These corrections appeared to be very small.

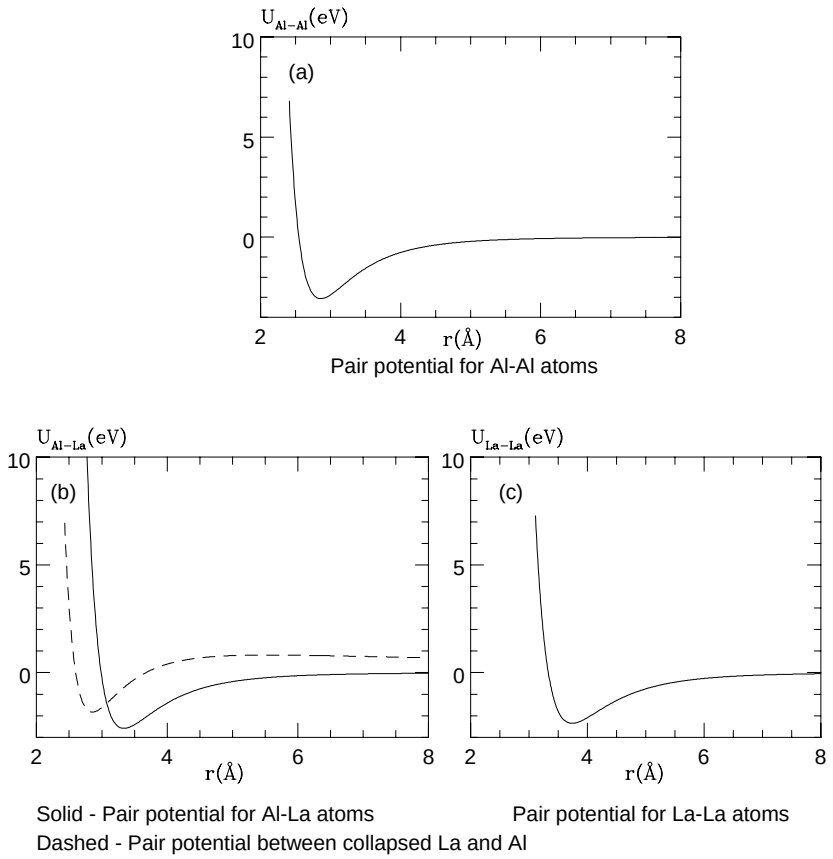

Figure 1. Three possible pair potentials are exhibited as functions of the separation distance of the pairs. One of these pair potentials (the Al–La one) changes its shape when the La atom collapses. (*a*) The pair potential for Al–Al atoms. (*b*) The pair potentials for Al–La (solid) and Al–$\mathrm{La_{coll}}$ (dashed) atoms. (*c*) The pair potential for La–La atoms.

Now the pair potential $U_{\mathrm{La-Al}}$ can take two possible shapes, depending on the state of the La atom:

$$U_{\mathrm{La-Al}} = \begin{cases} B_{\mathrm{La-Al}} r^{-12} - A_{\mathrm{La-Al}} r^{-6} & \text{(blown)} \\ B_{\mathrm{La^{coll}-Al}} r^{-12} - A_{\mathrm{La^{coll}-Al}} r^{-6} + \Delta E & \text{(collapsed).} \end{cases} \tag{2}$$

Here $\Delta E = 2$ eV is the increase of the La shell energy, caused by the transition from the blown to the collapsed state, whose value is taken from reference [7]. Four available pair potentials are exhibited in figure 1.

The simulation is carried out for 500 atoms (450 Al and 50 La atoms) packed in a cubic cell. Its dimension is chosen according to the experimentally measured density of the glass ($\rho = 3.35$ g cm^{-3} [11]). Special care is taken to ensure that the initial distributions of atoms do not contain La–Al pairs at distances smaller than 3.3 Å. The standard Monte Carlo

procedure [12] is realized for different temperatures. The periodic boundary conditions as described in [1] are implied.

In principle, at each step of the calculation random shifts of the atomic positions should be generated as well as possible transitions between the blown and collapsed states of the rare-earth atoms. This means that the coordinates and the atomic states are independent variables. However, there is a certain correlation between these for the following reasons:

(a) If the distance in a La–Al pair is more than 3.3 Å (the minimum of the potential (2) in the blown state) there is hardly any energy gain associated with the transition to the collapsed state. In this case the La–Al distance is larger than the sum of the effective radii of the two atoms and no structural changes are able to compensate for the 2 eV increase of the La atom energy due to the collapse.
(b) If this distance is smaller than 3.1 Å (see figure 1(*c*)) the blown state can hardly compete with the collapsed state. Then the La–Al distance is smaller than the sum of their radii (with the 'collapsed' radius for La) and the interaction in this pair becomes too large if the La atom converts back to the blown state.

We made an additional study of the influence of the value 3.1 Å on the average number of collapsed and deformed atoms. The simulations for the value 3.0 Å showed that no substantial changes happen. (The same is true for the upper value, 3.3 Å.) This correlation can be used to reduce the computation time by applying the following rules:

(a) All of the Al atoms are initially separated from their La counterparts by distances larger than 3.3 Å and all of the La atoms are in the blown state.
(b) All of the La atoms, whose closest Al neighbours are separated by distances larger than 3.3 Å, are always blown.
(c) If an Al atom approaches the La to a distance between 3.3 Å and 3.1 Å, the computer checks whether such a step is acceptable according to the Metropolis rule without a transition to the collapsed state. Only if the step is not acceptable is the possibility of the transition checked for the same configuration.
(d) When neighbouring Al atoms wander at distances 3.3 Å to 3.1 Å, the possibility of transition between blown and collapsed states is routinely checked.
(e) All of the La atoms which have Al neighbours at distances smaller than 3.1 Å are assumed to be in the collapsed state.

The average number of La atoms in the collapsed state is calculated as a function of temperature. There are also a certain number of La atoms in the blown state with Al neighbours at distances smaller than the minimum of their pair potential (<3.3 Å). These will be called in what follows 'deformed atoms' and their number, versus temperature, is also found. The averaging procedure does not take into account the states which are correlated with the initial configuration, which means that the averaging starts only after some necessary relaxation time. The corresponding number of Monte Carlo steps is estimated for different temperatures from the calculated value of the diffusion coefficient [13]. This number is chosen to be sufficient for a randomly diffusing atom to pass through the distance between two opposite walls. The averaging is done over a somewhat larger number of steps.

3. Results and discussion

3.1. Monte Carlo simulation results

As mentioned above, we start our simulation with zero collapsed and deformed La atoms, since none of them have Al neighbours closer than 3.3 Å. During the Monte Carlo process some Al

atoms approach the La atoms and may cause their conversion into a collapsed state.

As we have mentioned in [1], a local configuration contains one La atom and nine Al atoms†. It appears that the Al atoms which are in the majority in our system try to form a regular and possibly densely packed structure, but some important places are occupied by La atoms and prevent its formation. Nevertheless, the Al system tries to push its atoms into these occupied places at the expense of its own energy. Atomic collapse presents a new possibility for lowering the energy of the system, by decreasing the effective radius of the La atoms which is accounted for by the potential (2).

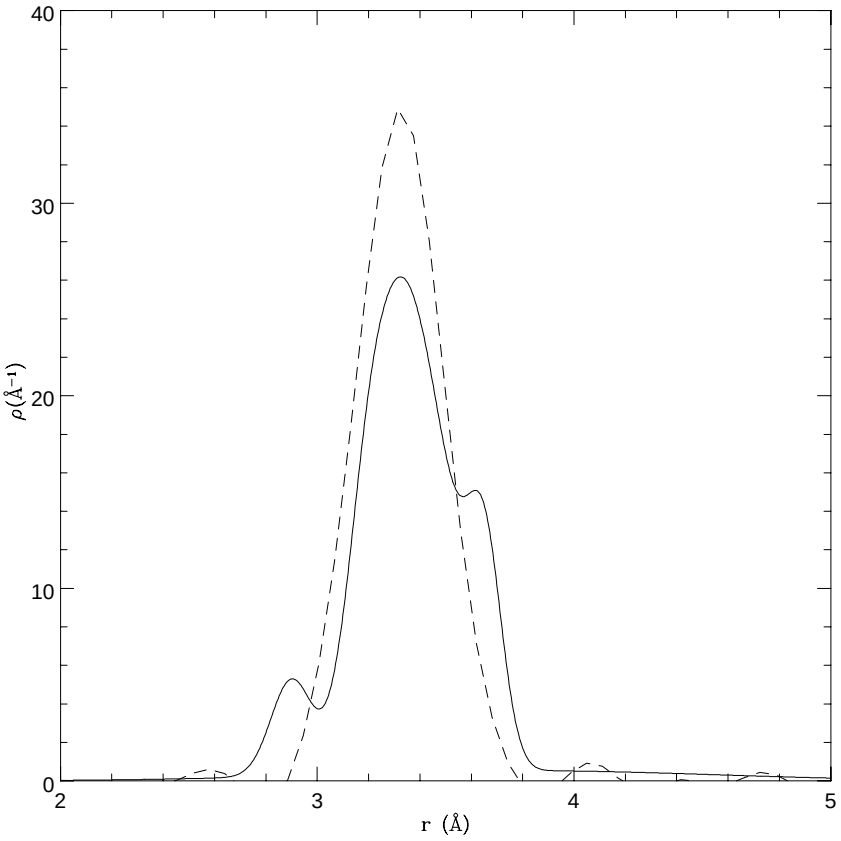

Figure 2. Radial distribution functions obtained by the splice method of XAFS [10] (dashed) and Monte Carlo simulations (solid). When comparing these two curves one should take into account that the experimental resolution is much lower than that achieved theoretically. Comparing the positions of the principal peak and relevant areas (as described in the text), the coincidence of the experiment and the theory is remarkable.

The RDF function plotted in figure 2 is clear confirmation of this statement. One can distinguish two peaks of the RDF function. The first small peak (the so-called prepeak) apparently corresponds to pairs of collapsed La–Al atoms separated by a distance of about 3.0 Å. When comparing the experimental and calculated RDFs, one should keep in mind that

† Reference [10] gives 14.5 as the number of atoms in the 'first coordination sphere'. To be more exact, this is the number of Al atoms lying at distances smaller than 4.1 Å from the La atom, which is in agreement with our simulation.

the experimental resolution is much lower than that achieved in calculation. The experimental curve is a sort of coarse-grained version of the theoretical one. Comparing the two curves, we want to emphasize a remarkable coincidence of two important parameters:

(a) The positions of the main peaks coincide nearly exactly.
(b) The coordination numbers, calculated as the areas under the RDF in the range up to the distances of about 4 Å, agree very well with the experimental value (14.5—theory; 14.5 ± 0.1—experiment); the areas under both theoretical and experimental RDFs up to distances smaller that 3.1 Å are close to 1.5. The latter number means that there is always one Al atom positioned anomalously close to each La atom, which is normally in a collapsed state.

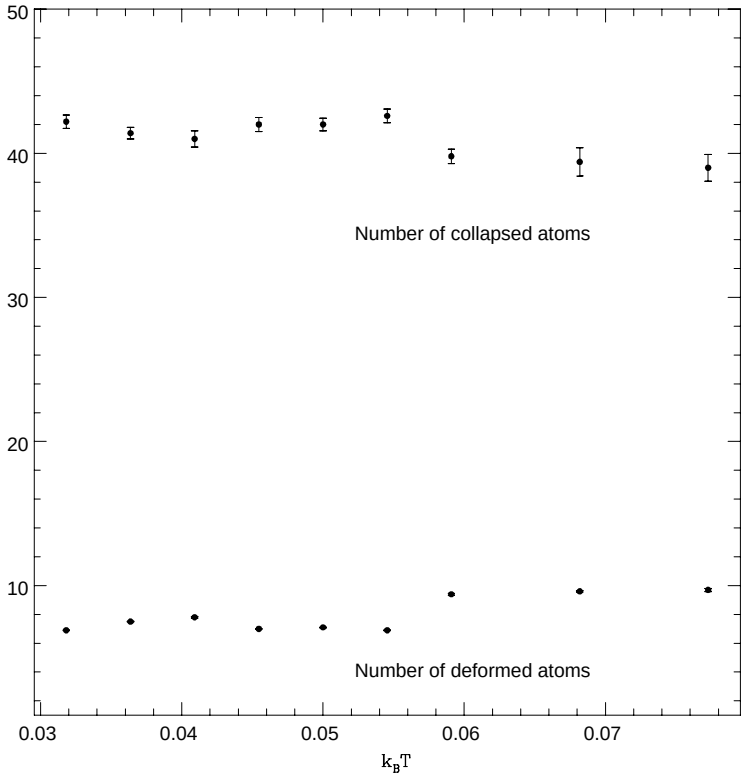

Figure 3. The dependence of the average number of collapsed and deformed atoms on the temperature. The number of collapsed atoms becomes smaller at higher temperature. However, this decrease is not as rapid as one may have expected since the simulations are carried out at a constant volume of the glassy system.

We calculate the average number of the deformed and collapsed La atoms in the temperature interval 350 K to 850 K. Figure 3 shows the dependence of the average number of collapsed and deformed atoms on the temperature. One can see that nearly all of the La atoms are either collapsed or deformed, which corresponds to our previous result on the anomalous approach [1]—a La atom has as a rule an Al counterpart which lies closer than the minimum of their pair potential (in the blown state). This exerts a certain ‘pressure’ on the corresponding

La atom and pushes it into the collapsed state. This causes a change in the La–Al pair potential and this Al atom is now better situated, at the minimum of the potential.

The average number of collapsed atoms decreases slowly with temperature. However, contrary to our intuitive expectations, the transition from collapsed to blown state with increasing temperature does not occur rapidly enough. It is worthwhile to draw attention to the fact that the simulations are carried out at constant volume rather than at constant pressure, which would have corresponded better to the normal experimental situation. When, at increased temperature, the La atoms tend to blow, the fixed volume of the system prevents them from doing this. This may be equivalent to a high external pressure applied to the sample, which might be useful if we want to realize such conditions experimentally.

In order to understand this aspect of our system in more detail, we carry out an additional simulation and calculate the pressure on the individual La atoms in 'blown' and 'collapsed' states for various temperatures. This pressure is calculated according to the technique described in [4]. The internal stress on the La atoms was defined as

$$\sigma_i^{\alpha\beta} = \frac{1}{2}\Omega_i \sum_j f_{i,j}^{\alpha} r_{i,j}^{\beta} \tag{3}$$

where Ω_i is the La-atom volume; $f_{i,j}$ and $r_{i,j}$ are the two-body force and the separation between the ith and jth atoms, respectively. Since amorphous alloys are macroscopically nearly isotropic, we can adopt the spherical representation and consider the average hydrostatic pressure as

$$p = \frac{1}{3}(\sigma^{xx} + \sigma^{yy} + \sigma^{zz}). \tag{4}$$

Figure 4 shows the dependence of the average pressure exerted on the collapsed La atoms on the system temperature, the averaging being done over all collapsed atoms. This pressure is negative in the temperature interval 300 to 600 K. This means that the La atoms attract the neighbouring Al atoms and stabilize the system by decreasing the total internal energy. At temperatures larger than 600 K, the average pressure on the collapsed La atoms becomes positive. All collapsed La atoms try to pass to their blown state and push the Al atoms away, thus increasing the volume of the system. This is, however, not possible since the volume of the system must remain constant during the simulation.

In the next subsection we will consider an equivalent Ising model with parameters deduced from the above simulations. It will allow us to bypass the problem of the constant volume and to arrive at some conclusions on the thermodynamic properties of our system.

3.2. The Ising model for Al-rich metallic glasses

The atomic collapse phenomenon seems to play an important part in the formation of the Al-rich metallic glasses, as has been demonstrated by the above simulations. The ability of the rare-earth atoms to be in one of two states—collapsed or blown—can be formally described by an iso-spin in an external field. This leads one to assume that a certain version of the Ising model

$$H = (1/2)\sum_{ij} I s_i s_j - h\sum_i s_i + Nc \tag{5}$$

may describe the thermodynamic properties of the Al-rich glass. The summation in the first sum in equation (5) is carried out only over the rare-earth atoms and includes only their nearest neighbours. N is the number of rare-earth atoms. The 'blown' and 'collapsed' states of each atom correspond to the up, $s = 1$, and down, $s = -1$, states of the iso-spin, respectively.

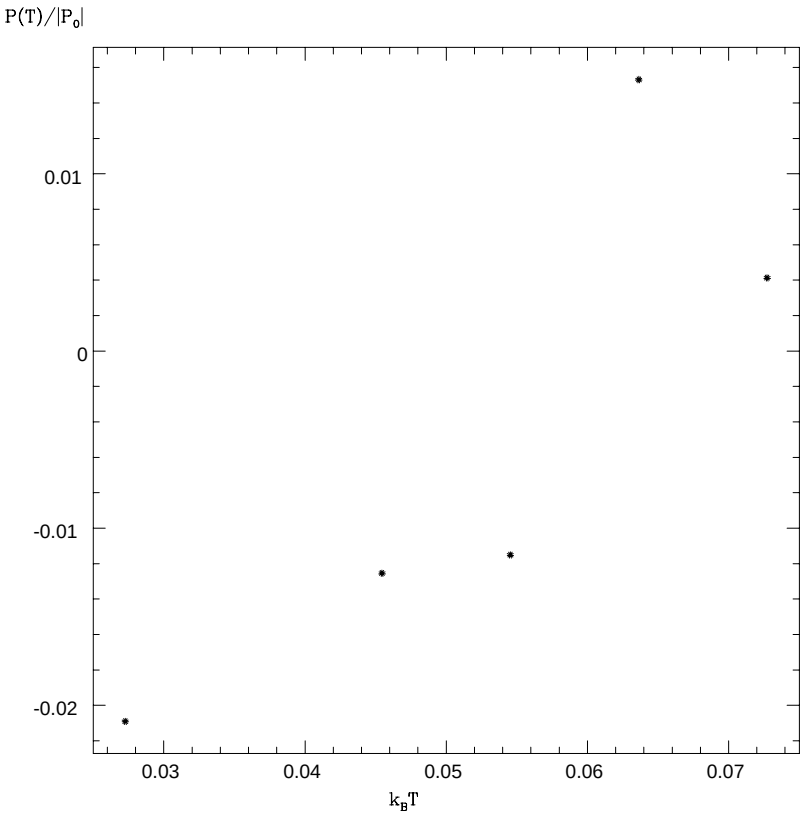

Figure 4. The dependence of the average pressure of the collapsed La atoms on the system temperature. This pressure increases with the temperature, indicating the tendency of atoms to decollapse—which is largely prevented by the volume of the system, which is kept constant.

The parameters in equation (5) can be found in the following way. First, consider a pair of rare-earth atoms, with the surrounding Al atoms. Their total energy depends on the state of the rare-earth atoms and may have any of three values $I_{\uparrow\uparrow}$, $I_{\downarrow\uparrow} = I_{\downarrow\uparrow}$, and $I_{\downarrow\downarrow}$. These energies should include the difference between the energies of the collapsed and blown atoms and the relaxation of the neighbouring Al atoms caused by the change of the rare-earth-atom radius.

The parameters of the Hamiltonian (5) are connected with the above three energies by the equations

$$I - 2h + c = I_{\uparrow\uparrow}$$
$$-I + c = I_{\uparrow\downarrow}$$
$$I + 2h + c = I_{\downarrow\downarrow}.$$

Thus

$$c = \frac{1}{4}(I_{\uparrow\uparrow} + I_{\downarrow\downarrow} + 2I_{\uparrow\downarrow})$$
$$I = \frac{1}{4}(I_{\uparrow\uparrow} + I_{\downarrow\downarrow} - 2I_{\uparrow\downarrow})$$

and

$$h = \frac{1}{4}(I_{\downarrow\downarrow} - I_{\uparrow\uparrow}).$$

$I_{\uparrow\uparrow}$ is the energy of a subsystem when two La atoms are blown, $I_{\downarrow\downarrow}$ that when two La atoms are collapsed, and $I_{\uparrow\downarrow}$ that when one of the La atoms is collapsed and the other one is blown. The computer calculations of the quantities $I_{\uparrow\uparrow}$, $I_{\downarrow\downarrow}$, and $I_{\uparrow\downarrow}$ were carried out using the Lennard-Jones potential as described in the previous section for several subsystems. Using the average values of these quantities, we estimated the parameter I to be negative and about -0.15 eV, meaning that the coupling between the iso-spins is of a ferromagnetic character. So the model has a tendency for spins to align. The 'effective magnetic field' h is about 0.01 eV.

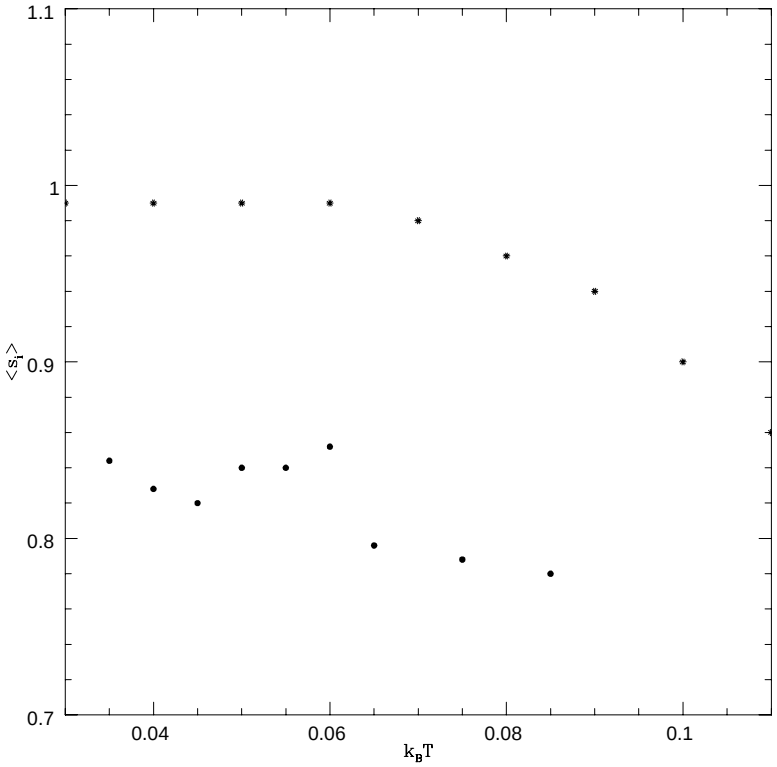

Figure 5. Comparison of the results for the temperature dependence of the average spin obtained by solving the effective Ising Hamiltonian (stars) and by Monte Carlo simulations (solid circles). One can see the difference between the behaviours of the average spin (average number of collapsed atoms) for the two models, which actually correspond to measuring this quantity at a constant volume or at a constant pressure, respectively.

The partition function for such a system

$$Z = \sum_{\{s_i = \pm 1\}} \exp\left[\beta\left(-(1/2)\sum_{ij} I_{ij} s_i s_j + h\sum_i s_i\right)\right] \tag{6}$$

can be calculated in the mean-field approximation when the thermal averaging of a spin value is given by means of the equation

$$\langle s_i \rangle = -\tanh\left[\beta\left(\sum_j I_{ij}\langle s_j\rangle - h\right)\right]. \tag{7}$$

Assuming that the average spin values $\langle s_i \rangle$ do not depend on i, equation (7) becomes

$$\langle s \rangle = \tanh[-\beta(zIs - h)] \tag{8}$$

where z is the coordination number (the number of the nearest-neighbouring La atoms, chosen to be six in our calculations).

This equation is solved numerically and figure 5 presents the dependence of the average iso-spin on the temperature. These results and the results of Monte Carlo simulations are presented in figure 5. One can see that our assumption of a stronger dependence of the average number of collapsed atoms on the temperature at constant pressure was correct. It is emphasized here that, although formally the volume of our Ising system does not change, the result presented here describes a system with variable volume. One can understand this from the fact that no restrictions have been placed on the rotation of the iso-spins. However, the states with up and down iso-spins correspond to La atoms with different volumes; hence the volume of the real physical system changes according to the proportion of up and down spins.

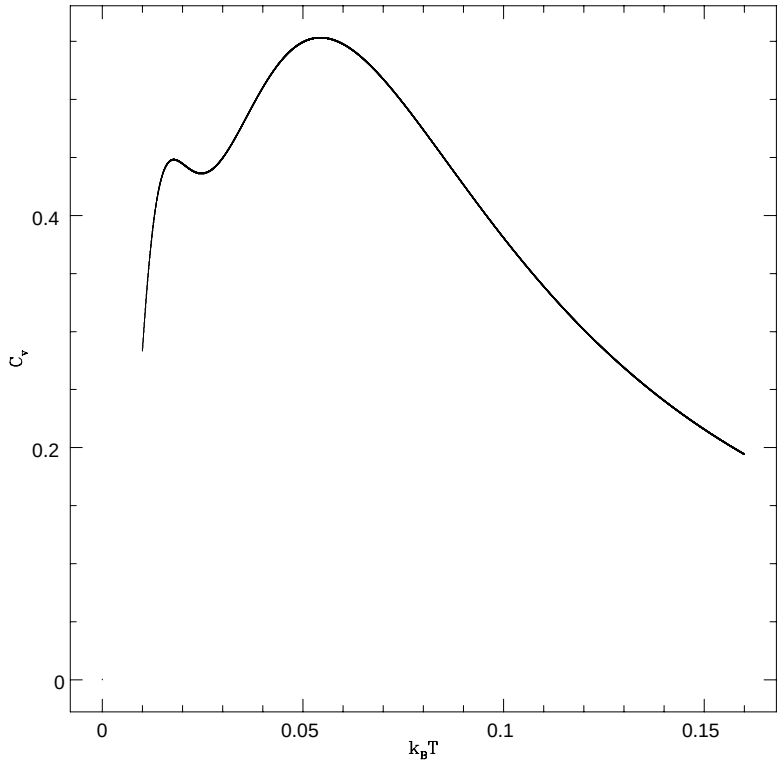

Figure 6. The dependence of the specific heat on the temperature, with two humps. The appearance of these humps is associated with the onset of spin flips, i.e. decollapse processes. One may assume that in this temperature region the glasses system loses it stability and a crystallization process (not accounted for by the Ising model) may commence.

3.3. Heat capacity

The paper [2] presents differential scanning calorimetric curves (DSC) of amorphous $Al_{100-x}La_x$ ($x = 7, 8, 9$ and 10) alloys which exhibit two exothermic peaks. The first

exothermic peak is observed at a temperature of about 500 K, whereas the second one shows up at about 600 K. These peaks are attributed to the precipitation of crystallites in the glass.

Using the mean-field variational approach to the Ising model, one can get an expression for the variational free energy (see, e.g., [14]). This is done by replacing the actual interaction between parts of the system by a fictitious interaction with some external field or potential. The Hamiltonian is then divided into two parts, $H = H_0 + H_1$, where H_0 is a trial Hamiltonian in which none of the system variables interacts with the effective external field. The interaction is characterized by the parameter λ, and the free energy is minimized with respect to λ. The result is

$$f_{var}(\lambda_{min}) = -(1/\beta)\ln[2\cosh(\beta\lambda_{min})] - (\lambda_{min} - h)^2/2z\epsilon \tag{9}$$

where λ_{min} is the solution of the equation

$$\lambda_{min} - h = z\epsilon\tanh(\beta\lambda_{min}). \tag{10}$$

Now it is a matter of standard calculations to find the specific heat C_v.

Figure 6 presents the dependence of C_v on the temperature. Two peaks in the heat capacity are clearly visible. We suppose that the first peak marks the temperature at which the La atoms transit from their 'collapsed' to 'blown' states. The second peak indicates that the iso-spins in the system become unbound. Near this region of temperatures the system absorbs most of the heat.

Since the model does not incorporate the possibility of crystallization, this curve cannot be directly compared with the above experiment. However, the decollapse of the La atoms predicted by the model clearly indicates a loss of stability of the glassy state and a possibility of crystallization. It is remarkable that the decollapse temperature region is close to the experimentally observed onset of crystallization.

4. Conclusions

This paper demonstrates how the rare-earth-atom collapse influences the formation and thermodynamics of Al-rich glasses. The collapse is introduced by means of a Lennard-Jones potential, constructed in such a way that two possible atomic states of La are taken into account. The standard Metropolis procedure is then applied for the calculation of the radial distribution function. The results are in agreement with the XAFS results on the radial distribution function [10]. The average numbers of deformed and collapsed La atoms are calculated, and the dependence of these values on the temperature is studied.

It is shown that the system can be described by an equivalent Ising Hamiltonian whose parameters are estimated on the basis of the above simulations. This Hamiltonian allows one to study some thermodynamic properties of Al-rich glasses in a straightforward fashion. We investigated the dependence of the average spin values $\langle s_i \rangle$ (describing two possible atomic states) on the temperature. The temperature dependence of the specific heat is also obtained in the mean-field approximation. The temperature at which La atoms start decollapsing is close to the temperature at which crystallization is observed experimentally [2].

All of this indicates the important part played be the rare-earth atomic collapse in the formation of the Al-rich metallic glasses and in their thermodynamics.

Acknowledgments

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