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# FERROMAGNETIC LIQUID DROPLETS

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An experimental evidence of ferromagnetic behavior of liquid droplets produced by laser ablation from amorphous alloys is presented for the first time. Thin films of amorphous magnetic materials were fabricated by laser deposition technique in the presence and in the absence of magnetic field. The difference in parameters of deposited films is attributed to ferromagnetic properties of small size liquid droplets.

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Exchange energy is typically smaller than energy of direct Coulomb interactions of ions and for this reason the liquid state of a ferromagnetic material can not be ferromagnetic. A metastable ferromagnetic liquid can be produced by supercooling of a ferromagnetic material to a temperature smaller than the Curie temperature [1]. More interesting is another possibility which comes from the facts that the melting temperature of particles strongly decreases with the decrease of a particle size for small-sized particles [2], meanwhile the Curie temperature shows only a slight variation with the change in a particle size [3]. Thus, sufficiently small liquid particles of a ferromagnetic material with the Curie temperature close to the melting temperature should be ferromagnetic. Here we present experimental evidence in favor of ferromagnetic behavior of liquid droplets produced during laser ablation [4] of amorphous magnetic materials in the presence of a magnet.

The experimental installation and procedures are described in details in [5]. We deposited amorphous ribbons of the atomic composition $Fe_{67}Co_{18}Si_1B_{14}$ and a bulk amorphous material of the composition $Fe_{4.35}Co_{68.15}Si_{12.5}B_{15}$ by means of laser ablation technique. The deposition was done in vacuum of about $10^{-7}$ mbar on silicon $p$-type substrates of the orientation (1,0,0). Two samples were produced during each deposition cycle: one was fabricated at the substrate with a strong magnet placed behind the substrate and the other – without the magnet. The magnet axis was perpendicular to the substrate surface. A distance of 15 cm separated these two samples and the magnet did not affect the deposition of the second sample.

The samples were analyzed by scanning electron microscopy, Auger electron spectroscopy, profilometry and magnetometry. An ensemble of droplets produced during laser ablation [4] was detected at the surface of the deposited films. The droplets were distributed with the concentration of $10^4 - 10^6$ $1/cm^2$, and a size range from several tens nanometers up to several micrometers. The droplet composition was close to that of the film.

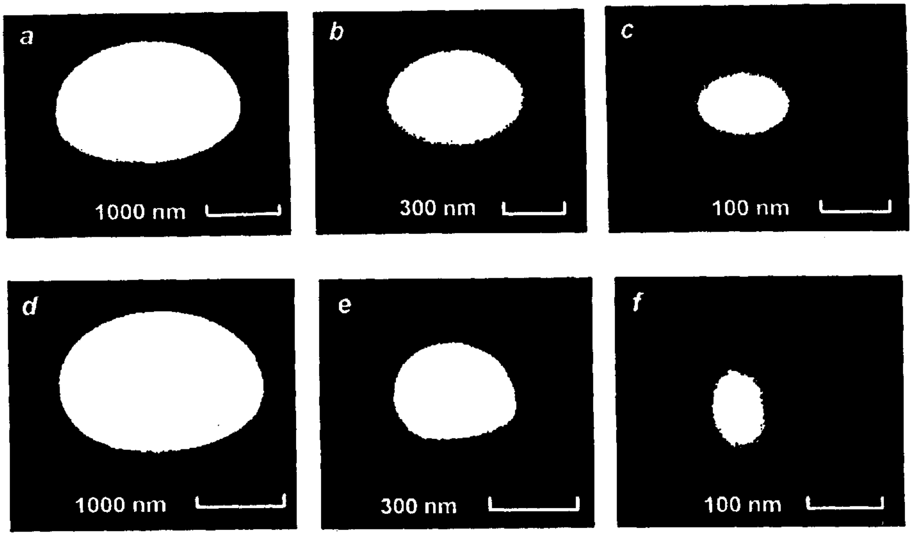

Fig.1. Scanning electron images of the film surface with droplets of different sizes investigated under the flat angle of 45°: $a - c$ were taken for the sample produced without the magnet, $d - f$ were measured for the sample fabricated with the magnet. The images contrast is high in order to emphasize the droplet contours

We found interesting peculiarities of a droplet geometrical form. The geometrical form of droplets on films deposited without the magnet was not changed with the reduction of the droplet size, while the geometrical form of droplets, produced in the presence of the magnet, showed a strong size dependence. Droplets, which had dimensions smaller than some critical size, stretched along the direction of magnetic field and the ratio of the droplet height $h$ to the droplet diameter $d$ (an aspect ratio) increased from the value of 0.1 for large-sized droplets (evaluated by means of profilometry) to the value of 1-2 for small-sized droplets (measured by electron microscopy). Fig.1 shows three typical pairs of droplets of different sizes measured by means of a scanning electron microscope. Images $a - c$ correspond to the sample prepared without the magnet, $d - f$ correspond to the sample fabricated with the magnet. In order to evaluate the ratio of the droplet height to the droplet diameter, these images were taken under an angle of 45° relative to the substrate surface, see Fig.2 (the droplet images measured under the normal incidence of the electron beam were circles). Fig.2 demonstrates how the aspect ratio ($> 0.22$) can be evaluated from the droplet tilt images. For droplets with small aspect ratios the projection image should be an ellipse with the axes ratio 0.7. We observed this ratio for all droplets on the films produced without the magnet and for large size droplets on the films deposited with the magnet. However, the axis ratios of the projection image of small-sized droplets (with the projection diameter smaller than 300 nm) at the films fabricated with the magnet were greater than 0.7. Then, simple geometry indicates that the ratio of the droplet height to the diameter for small-sized droplets is much higher than that of large-sized droplets. The aspect ratio for the droplet e with diameter of 300 nm can be roughly evaluated as 0.7 and for the droplet $f$ with diameter of 70 nm as 1.5.

The ferromagnetic nature of small-sized droplets is the most probable explanation of the observed change of the droplet geometrical form. It is clear that a minimum of a

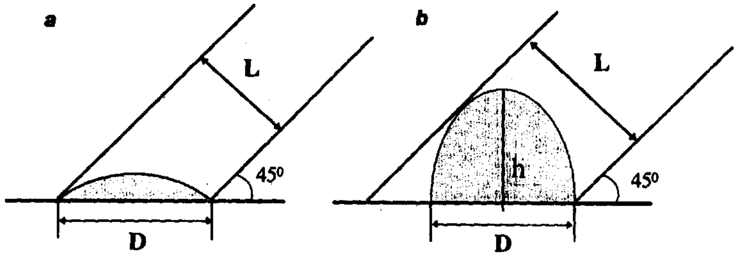

Fig.2. Schematic diagrams of measurements of the droplet aspect ratio: *a* – a droplet with a small ratio of the droplet height to diameter, *b* – a droplet with a high ratio of the droplet height to diameter

magnetic energy of a ferromagnetic droplet placed in strong homogeneous magnetic field requires a high aspect ratio, meanwhile a minimum of the surface energy results in a small aspect ratio, which is governed by surface energies. The higher the droplet magnetization is, the higher the aspect ratio will be observed. Since all studied droplets have a circular projection at the surface (large droplets were sphere segments), it means that they were liquid when they became ferromagnetic. The ferromagnetic properties of droplets can be explained by the size dependence of the melting temperature or/and supercooling of droplets. The melting temperature of a particle can be estimated from a comparison of surface and volume energies as

$$T = T_{mb} - C\frac{\sigma_s - \sigma_l}{(c_s - c_l)\rho h}, \tag{1}$$

where $T_{mb}$ is the melting temperature of the bulk, $C$ is the constant which depends upon the particle geometry and reflects the surface-to-volume dimensionless ratio, $\sigma_s$ and $\sigma_l$ are surface energies of solid and liquid states respectively, $c_s$ and $c_l$ are thermocapacity of solid and liquid states, $\rho$ is the density of the material and $h$ is the characteristic particle size. For example, for cobalt flat droplets the values are as follows: $\Delta c = c_s - c_l = 10^5\,\mathrm{erg/g{\cdot}K}$, $\Delta\sigma = \sigma_s - \sigma_l = 200\,\mathrm{erg/cm^2}$, $\rho = 8.9\,\mathrm{g/cm^3}$, the droplet height is the characteristic particle size and the coefficient $C = 4$. Taking $h = 20\,\mathrm{nm}$, we get for $\Delta T = T_{mb} - T =$ $= 300\,\mathrm{K}$, which is close to the difference between the Curie temperature $T_c = 1388\,\mathrm{K}$ and the bulk melting temperature $T_{mb} = 1765\,\mathrm{K}$ of cobalt ($T_{mb} - T_c = 377\,\mathrm{K}$). In favor of the size dependence of the melting temperature also says the fact that smaller droplets manifest greater magnetic properties (higher aspect ratios). Indeed, magnetization near the Curie temperature strongly depends upon the temperature. A droplet of a smaller size has a lower melting temperature, which results in higher magnetization.

To check the ferromagnetic nature of small-sized droplets we performed a test deposition of the amorphous bulk material, in which the magnet axis was parallel to the substrate and the magnet was placed behind the substrate at the distance of 1 cm from its center. As a result, an in-plane magnetic field was generated at the surface and a deflection force acted on magnetic particles. We found no deviation of droplets in respect with the position of the deposition spot. It means that during the flight from the target to the substrate the droplets had a temperature higher than the Curie temperature and acquired magnetic properties at the substrate surface. Again we observed a difference in the geometrical form of large-sized and small-sized droplets. Fig.3 shows electron microscopy images of two droplets of different sizes (the film surface was perpendicular to

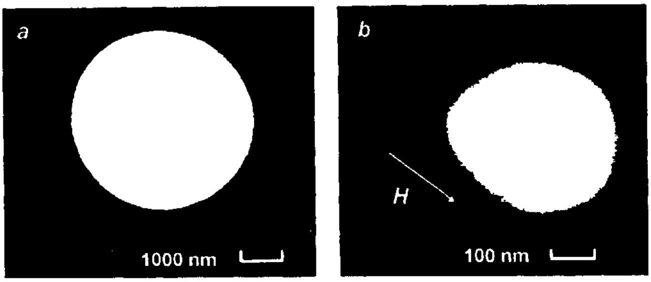

Fig.3. Scanning electron images of droplets taken under the normal angle of incidence of the electron beam at the film deposited in the presence of an in-plane magnetic field **H**: *a* – large-sized droplet, *b* – small-sized droplet

the electron beam). The large-sized droplet *a* has a circular form, meanwhile the small-sized droplet *b* has a form close to that of an ellipse with the long axis along the direction of the in-plane magnetic field. Such a form should be expected for a droplet that becomes ferromagnetic in a molten state during the process of cooling.

In conclusion, changes of the geometrical form of the droplets produced by laser ablation of amorphous alloys in the presence of magnetic field are strong evidence in favor of the fact that we observe for the first time a ferromagnetic liquid state of laser ablated small-sized droplets of a ferromagnetic material. This liquid ferromagnetic state can arise due to size dependence of the melting temperature of small objects and due to droplet supercooling. The discovered effect can be useful for production of magnetic nanoobjects and quantum dots.

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1. A.Inoue and A. Katsuya, Jap. J.: Mat. Trans. JIM **37**, 1332 (1996).
2. P.M.Ajayan and L.D.Marks, Phys. Rev. Lett. **63**, 279 (1989).
3. M.Godinho, J.L.Dormann, M.Nogues et al., J. Magn. Magn. Mater. **144**, 369 (1995).
4. G.Koren, A.Gupta, R.J.Baseman et al., Appl. Phys. Lett. **55**, 2450 (1989).
5. P.I.Nikitin, A.A.Beloglazov, A.Yu.Toporov et al., J. Appl. Phys. **82**(3), 1408 (1997).