

MÖSSBAUER EFFECT STUDY OF Fe GRAINS IN NANOCOMPOSITES

Nanocrystalline Alloys and Multilayers

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Abstract: The magnetic properties of Fe grains were studied by Mössbauer spectroscopy in three different nanocomposite systems: Fe-Zr-B-Cu nanocrystalline alloys prepared from melt quenched amorphous precursors, and Fe/B and Fe/Ag multilayers prepared by vacuum evaporation. It is shown that non-equilibrium alloying plays an overwhelming role in the deviation of the value of the Fe hyperfine field in small particles and in the bulk. On the other hand, a grain boundary phase with distinct magnetic properties cannot be separated. With decreasing grain size the superparamagnetic behaviour of the Fe grains becomes more dominant and a coexistence of ferromagnetic and superparamagnetic particles can be observed. Multilayer deposition is shown to be a flexible tool for preparing magnetically heterogeneous nanocomposite structures with narrow size distributions, offering new possibilities to study the magnetic interactions between nanosize objects.

1. INTRODUCTION

Nanocrystalline Fe (nc-Fe) has been the subject of many studies since the eighties when different technologies were developed to prepare it either as a single phase material or as a part of a nanocomposite. Many of its peculiar properties were attributed to a special grain boundary structure which is very different from that of the usual grain boundaries in polycrystalline materials. The Gleiter model of nanocrystalline materials [1] depicted them as essentially perfect fine grains with wide disordered grain boundaries of significantly reduced density. Mössbauer spectroscopy gave an essential contribution to this model, providing measurements on nc-Fe prepared by the inert gas condensation technique [2]. The results were described by two hyperfine components: a sharp sextet with parameters of pure bcc-Fe (crystalline component) and a broad sextet (grain-boundary component) with different parameters. The temperature depend-

ence of the broad sextet and the sharp lines was found to be different and an increased magnetic moment (*i.e.* low temperature hyperfine field) of the grain boundary component was also observed. However, more recent Mössbauer effect studies on nc-Fe prepared by other methods could not reproduce this feature and a component in the Mössbauer spectra corresponding to grain boundary atoms could not be identified [3]. Studies of nc-Fe in polycrystalline Fe/B multilayers [4] led to the conclusion that the perturbation which can be found in the hyperfine field due to changes of the Fe coordination numbers and distances in bcc-grain boundaries is of the order of the experimental linewidth (*i.e.* below 1 T). In this work we will study three nanocomposite systems, where the grain size is sufficiently small for superparamagnetic behaviour of the grains. We will also examine questions concerning the grain boundary phase and interaction between nanosize particles.

2. EXPERIMENTAL

2.1. Fe-Zr-B-Cu nanocrystalline alloys

NANOPERM type $\text{Fe}_{92-x}\text{Zr}_7\text{B}_x\text{Cu}_1$ nanocrystalline alloys (nc- $\text{Fe}_{92-x}\text{Zr}_7\text{B}_x\text{Cu}_1$) were prepared from melt quenched amorphous ribbons by heat treatment in a differential scanning calorimeter (DSC) to a well defined stage of the crystalline transformation.

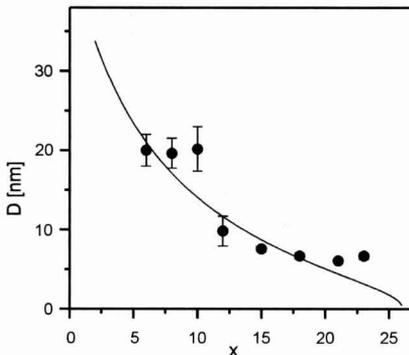


Figure 1. Composition dependence of the bcc-Fe grain size in nc- $\text{Fe}_{92-x}\text{Zr}_7\text{B}_x\text{Cu}_1$

The average grain size of the bcc-Fe phase was measured by X-ray diffraction [5]. The composition dependence of the grain size after a heat treatment to the end of

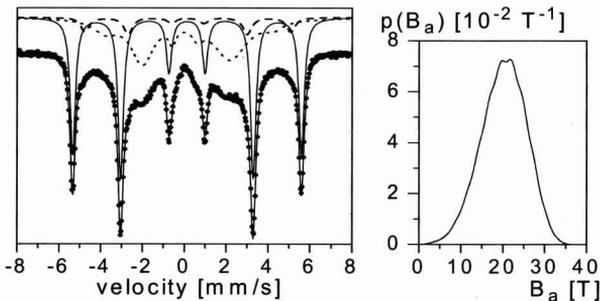


Figure 2. Mössbauer spectrum of the nc- $\text{Fe}_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ composite measured at 12 K. The fitted subspectra (see text) are also shown. The evaluated hyperfine field distribution of the residual amorphous phase is shown in the right panel

the first crystallization peak is shown in Fig. 1. The solid line represents an estimate based on the amount of the bcc-phase [5]. The data, evaluated using Rietveld full-profile matching, applying the FULLPROF program, confirm that in the first transformation stage nanosized bcc-grains are precipitated in the amorphous matrix. A typical Mössbauer spectrum and its evaluation is illustrated in Fig. 2. The spectrum consists of three basic components: the first one is a sharp sextet with parameters of bulk bcc-Fe (solid line), the second one is a broader sextet with a lower hyperfine field and smaller intensity (dashed line) and the third one is a broad hyperfine field distribution (dotted line). A hyperfine field higher than 33.8 T, *i.e.* that of bulk bcc-Fe at a low temperature, could not be observed, either in this spectrum measured at 12 K or in other measurements made at 4.2 K [5]. Based on a detailed study of the temperature dependence of the parameters [5], the three components were identified as follows:

- (i) Fe atoms in the bcc-phase with no impurities among the nearest or next nearest neighbouring atoms,
- (ii) Fe atoms in the bcc-phase with Zr and / or B impurity atoms in the first two coordination shells,
- (iii) Fe atoms in the amorphous matrix.

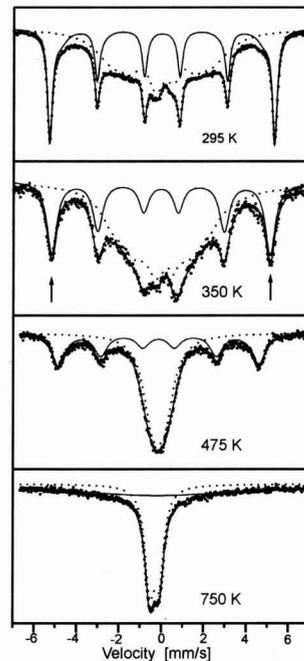


Figure 3. Temperature dependence of the Mössbauer spectra of nc-Fe₇₄Zr₇B₁₈Cu₁. The full and dotted lines show the subspectra belonging to the bcc and the residual amorphous phase, respectively. The broadening of the bcc-Fe lines can be clearly observed (see the lines indicated by the arrows) at 350 K

Although in literature [6] it has been claimed that the second component belongs to Fe atoms in grain boundaries, the temperature dependence of the hyperfine fields contradicts such an assignment. Neither an increased magnetic moment nor a faster decrease of the hyperfine field of the component in question could be observed, *i.e.* there is no indication for extended regions of significantly reduced density. Assuming

the existence of a non-equilibrium (few atomic percent) impurity concentration in the bcc phase does not contradict other microscopic measurements [7] and consistently describes [5] the observed concentration and temperature dependence of the parameters.

When the Fe concentration of the precursor amorphous phase is decreased (*i.e.* the B concentration is increased in our case), the size of the precipitated bcc-Fe grains decreases for samples that have been heat treated up to the end of the first crystallization peak (see Fig. 1). When the grain size is below 10 nm, a superparamagnetic relaxation typical of single domain particles can be observed at sufficiently low temperatures where the sample structure remains unaltered (*i.e.* below the first crystallization peak). Superparamagnetic behaviour of the bcc-Fe grains could be observed for $x = 12$ by Mössbauer spectroscopy [8] above the Curie temperature of the residual amorphous phase. The anomalous temperature dependence of the coercivity observed in various nanocrystalline systems [9] was explained by the appearance of superparamagnetism through a magnetic decoupling of the bcc-Fe grains taking place at or above the magnetic transition temperature of the amorphous intergranular region. However, the Mössbauer effect measurements for the $x = 18$ sample, which has small grain size (7 nm) and low bcc-Fe fraction (40%), contradict this simple picture. The Curie temperature of the amorphous phase is around 430 K, as determined from the temperature dependence of the hyperfine fields [5] measured below this temperature. The Mössbauer spectra at a few characteristic temperatures are shown in Fig. 3. The superparamagnetic relaxation of the bcc-grains is quite evident at 750 K, where no well resolved sextet can be observed in the spectrum, but the broadening of the sextet already starts at 350 K (the outermost lines of the sextet are indicated by arrows in Fig. 3), where the amorphous matrix has an average hyperfine field around 10 T. This points to the existence of a limiting value for the strength of the coupling mediated by the intergranular amorphous matrix [9] and supports calculations [10] indicating that dipolar interactions cannot be neglected when considering the magnetic behaviour of nanoscale magnets.

2.2. Fe / B multilayers

Multilayered samples were evaporated by electron guns onto Si single crystal or Al substrates in a vacuum of 10^{-7} Pa. The substrate was cooled by liquid nitrogen and the layer thickness was controlled by a quartz oscillator. Although the mutual solubility of the components is very low, both Mössbauer spectroscopy and transmission electron microscopy (TEM) indicated the formation of a non-equilibrium amorphous alloy [4] at the interface of the Fe and B layers. While the individual layers were found to be continuous with a thickness variation less than 1 nm, a columnar microstructure can be clearly observed in all samples and the planar grain size was found to scale with the layer thickness [11]. In this way the system is a composite structure with elements very similar to those of thermally nanocrystallized amorphous alloys, *i.e.* nanosize bcc-Fe and amorphous alloy grains. The main differences, when compared to the previously described nanocrystalline $\text{Fe}_{92-x}\text{Zr}_7\text{B}_x\text{Cu}_1$ alloys, are the chemical composition of the amorphous phase and the geometrical arrangement of the bcc-Fe grains.

The Mössbauer spectra of samples with varying Fe and B layer thickness could be consistently described [4] by two components: a sharp sextet of pure bcc-Fe and a broad

hyperfine field distribution of the amorphous interface. A spectrum measured at 4.2 K in a 3 T magnetic field applied parallel to the γ -ray direction is shown in Fig. 4. The component belonging to bcc-Fe is indicated by the dotted line. The line intensities are 3:0:1:1:0:3, since they depend on the angle θ between the γ -ray and the magnetic moment – aligned by the 3 T external magnetic field – as $3:x:1:1:x:3$ where $x = 4\sin^2(\theta) / (1 + \cos^2(\theta))$. A hyperfine field higher than that of pure bcc-Fe was not observed. This is in line with the measurements at ambient temperature [4], where neither a low field shoulder of the sharp sextet nor significant line broadening could be observed. Only for the sample with the $d_{\text{Fe}} = 2.5$ nm Fe layer thickness shown in Fig. 4, the linewidth of the bcc-Fe sextet (0.36 ± 0.02 mm/s) exceeded the experimental linewidth. The average thickness of the pure bcc-Fe layer is only about 0.5 nm in this sample, *i.e.* a few atomic layers, when taking into account the interface formation (around 2 nm). These experimental results impose a lower limit (around 1 T) for the variation of the hyperfine field due to perturbations in the coordination number and atomic distances in grain boundary regions.

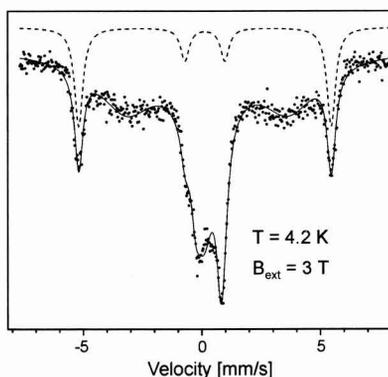


Figure 4. Mössbauer spectra measured at 4.2 K in a 3 T magnetic field applied parallel to the γ -ray direction for an Fe / B multilayer on an Al substrate with $d_{\text{Fe}} = 2.5$ nm and $d_{\text{B}} = 2$ nm layer thickness. The dashed line indicates the sub-spectrum belonging to the bcc-Fe grains

The continuous in-plane geometrical arrangement of the bcc-Fe grains is well reflected by the Mössbauer spectra (see Fig. 2 in [4]). The line intensities of the six-line pattern were 3:4:1:1:4:3, indicating that the magnetic moments lie in the sample plane. Superparamagnetic relaxation was not observed for any of the samples. These results show that the geometrical arrangement of the grains has a strong influence on the magnetic properties of nanometer size particles, underlying the role of dipolar interactions in the magnetic coupling.

2.3. Fe / Ag multilayers

The samples were deposited onto Si single crystal substrates without cooling. A sample with a 0.1 nm Fe thickness and with ^{57}Fe enrichment was prepared using the molecular beam epitaxy (MBE) equipment at the K.U. Leuven. Fe and Ag have a positive heat of mixing even in the liquid phase, implying that no interdiffusion is expected between the layers. Therefore, one may hope to learn more about the properties of chemically pure grain boundaries by studying these multilayers.

For layer thickness in the range $d_{\text{Fe}} > 1$ nm, continuous ferromagnetic Fe layers were found [12] and the smaller hyperfine field components that appear when d_{Fe} approaches 1 nm, are similar to those [13] attributed to Fe atoms at different sites of a stepped Fe / Ag interface.

When $d_{\text{Fe}} < 1$ nm the layers become discontinuous and the samples are partially or fully superparamagnetic at room temperature, as illustrated for three samples in Fig. 5. The blocking temperature of these granular alloys – roughly proportional to the average volume of the magnetic particles [14] – is very different for the three samples. For the $d_{\text{Fe}} = 0.7$ nm sample, it should be well above room temperature. For the $d_{\text{Fe}} = 0.4$ nm and 0.2 nm samples it is around room temperature and 40 K [12], respectively. The Mössbauer spectra of these samples measured at 4.2 K are also shown in Fig. 5. The spectra were evaluated by fitting a binomial distribution of the hyperfine fields [15] and the fitted distributions are also shown in the figure. The spectra are rather similar and there is no specific feature that can be assigned to an increasing number of grain boundary atoms when the grain size decreases. The average hyperfine field, indicated in the figure, is significantly larger than that of pure bcc-Fe (33.8 T) and the slight increase of the width of the distribution is close to the experimental error. The small intensity of the second and fifth line of the magnetically split sextets seems to be a characteristic feature of these kind of granular samples. It indicates that the magnetic moments are oriented more and more perpendicular to the sample plane when the layers become discontinuous. The average angle does not depend on the temperature, as confirmed for the $d_{\text{Fe}} = 0.7$ nm sample in Fig. 5 and also shown in [12] for a $d_{\text{Fe}} = 0.2$ nm sample. The most plausible explanation seems to be a shape anisotropy due to non-spherical granules. The formation of Fe nanoparticles with an elongated shape along the growth direction were observed before for BN / Fe discontinuous multilayers [16].

Granular alloys are usually magnetically heterogeneous systems at elevated temperatures, due to an unavoidable grain size distribution and the corresponding

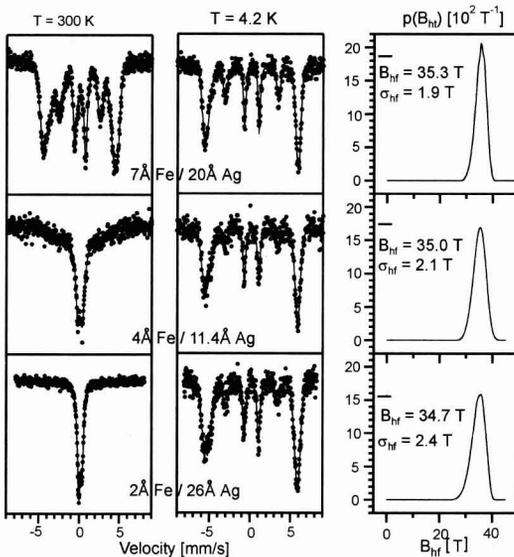
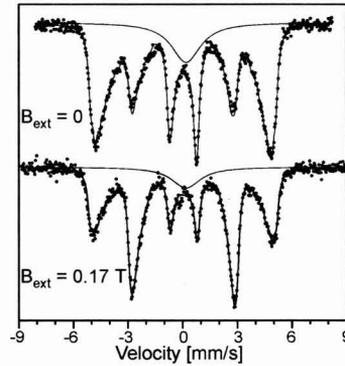


Figure 5. Mössbauer spectra of Fe / Ag multilayers with the indicated nominal layer thickness measured at 300 K and 4.2 K. The hyperfine field distributions fitted to the low temperature spectra are shown on the right

Figure 6. Mössbauer spectra of a [0.2 nm Fe / 0.6 nm Ag]₃₂₄ multilayer measured at 300 K with and without a small magnetic field applied parallel to the sample plane. The fitted paramagnetic subspectra are indicated



distribution of blocking temperatures. This is illustrated for a sample with a layer sequence [0.2 nm Fe / 0.6 nm Ag]₃₂₄ corresponding to an average Fe concentration of 34 at%, which is around the percolation limit. The room temperature Mössbauer spectra – measured with and without a small external magnetic field applied parallel to the sample plane – are shown in Fig. 6. The majority of the magnetic moments behaves like a ferromagnet and are aligned parallel to the sample plane by the small applied field. However, there is a smaller paramagnetic fraction – the respective subspectra are shown in Fig. 6 – which is only slightly reduced (from 17 to 12%) when the 0.17 T magnetic field is applied. This result is in agreement with SQUID magnetization measurements [12] on this sample, revealing a mixture of ferromagnetic and super

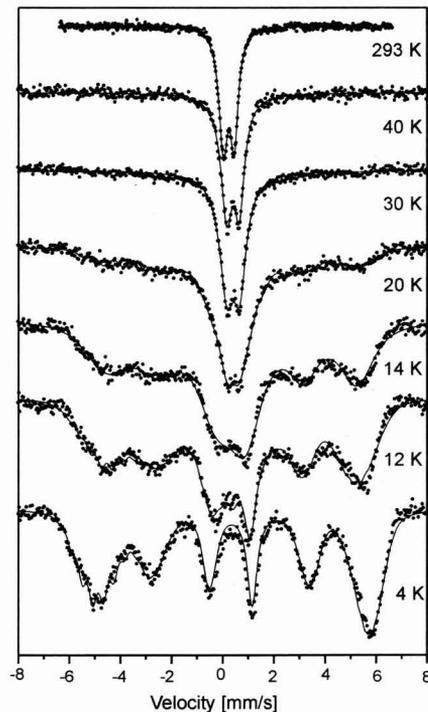


Figure 7. Mössbauer spectra of a [0.1 nm ⁵⁷Fe / 1.3 nm Ag]₇₅ multilayer measured at the indicated temperatures

paramagnetic phases at room temperature. It is remarkable that the average hyperfine field of the ferromagnetic component is quite large (28 ± 0.4 T) and the Ag grain size is around a few nm, as indicated by X-ray diffraction [12].

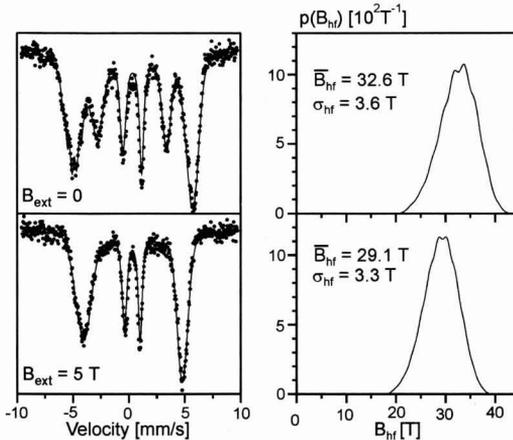


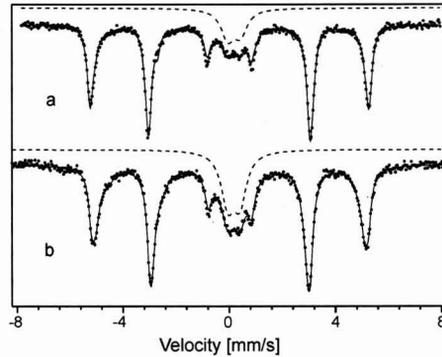
Figure 8. Mössbauer spectra and the fitted hyperfine field distribution of $[0.1 \text{ nm } ^{57}\text{Fe} / 1.3 \text{ nm Ag}]_{75}$ multilayer at 4.2 K with and without an external magnetic field as indicated in the figure

When studying the properties of small particles, discontinuous multilayers are advantageous, because in this way samples with small average grain size and narrow size distribution can be prepared. This is illustrated on a sample prepared by MBE with the following nominal layer sequence: 1.5 nm Ag / $[0.1 \text{ nm } ^{57}\text{Fe} / 1.3 \text{ nm Ag}]_{75} / 3.7 \text{ nm Ag}$. The Mössbauer spectra measured at different temperatures are shown in Fig. 7. Around 30 K an appreciable broadening of the paramagnetic lines can be observed, while the blocking temperature, where the ratio of the magnetically split component reaches 50%, is at 17 K. A comparison with results in literature [17] allows to estimate the grain size distribution, where the average is around 2 nm and the width is less than 1 nm. At 4.2 K the average hyperfine field (see the evaluated distribution and the parameters in Fig. 8) is smaller and the width of the distribution is significantly larger than that of the samples with higher blocking temperatures. To check whether this is a consequence of a relaxation behaviour or whether it results from a static hyperfine field distribution, the sample was measured in a 5 T magnetic field. The measured spectra and the calculated hyperfine field distributions are shown in Fig. 8. The applied field (which is now perpendicular to the sample plain, implying that $I_{2-5} = 0$) does not significantly affect the width of the distribution and the hyperfine field is reduced, as expected for a ferromagnetic sample. This shows that at 2 K the majority of the particles are in the blocked state. Therefore, the observed hyperfine field distribution is characteristic of structural or chemical differences around the Fe atoms. On the other hand, the hyperfine field is significantly different from that observed in nanocrystalline Fe [2, 3]. The large isomer shift (0.24 mm/s) and quadrupole splitting (0.43 mm/s) observed at 300 K and the lack of any well resolved component with the parameters of pure bcc-Fe at 4.2 K, hints an explanation that the superparamagnetic grains are not pure bcc-Fe grains.

The possibility to prepare samples with a controllable structure of the magnetic heterogeneities is a further advantage of the multilayer deposition. The Mössbauer

spectra of two multilayer heterostructures with varying thickness of the magnetic layer is shown in Fig. 9. The 0.2 nm thick Fe layers remain superparamagnetic at room temperature when embedded in between the thicker ferromagnetic Fe layers. The intensity ratios of the paramagnetic and magnetically split components agree well with the nominal ratio of the thin and the thick Fe layers. Preliminary results on the temperature dependence of the Mössbauer spectra indicate that the blocking temperature of the granular layers does not change significantly, but is more smeared out in the hetero-

Figure 9. Room temperature Mössbauer spectra of multilayer heterostructures with 2.6 nm Ag and varying Fe nominal layer thickness: $[[\text{Ag}/\text{Fe}(0.2\text{ nm})]_3/[\text{Ag}/\text{Fe}(3\text{ nm})]_{32}]$ (a) and $[[\text{Ag}/\text{Fe}(0.2\text{ nm})]_3/[\text{Ag}/\text{Fe}(1.5\text{ nm})]_{32}]$ (b)



structure than in the simple granular multilayer. The magnetoresistance of heterostructured multilayers [17, 18] is a topic of current interest.

3. CONCLUSIONS

Non-equilibrium alloying of Fe is observed in all the nanocomposite structures studied, *i.e.* in $\text{Fe}_{92-x}\text{Zr}_7\text{B}_x\text{Cu}_1$ nanocrystalline alloys prepared from melt quenched amorphous precursors, and in Fe/B and Fe/Ag multilayers prepared by vacuum evaporation. Due to the mixing a separate grain boundary component, *i.e.* a variation of the hyperfine field solely due to perturbations in the coordination numbers and atomic distances, cannot be separated.

Magnetic decoupling of superparamagnetic grains from a ferromagnetic matrix, observed both in $\text{Fe}_{92-x}\text{Zr}_7\text{B}_x\text{Cu}_1$ nanocrystalline alloys and in Fe/Ag granular multilayers, reveals that the strength of coupling mediated by a non-magnetic or ferromagnetic matrix is small. The observed perpendicular anisotropy in granular films indicates that magnetostatic energies and dipole interactions play a dominant role in the magnetic properties of nanocomposites.

Multilayer deposition was shown to be a flexible tool to prepare magnetically heterogeneous nanocomposite structures with narrow size distributions.

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