Self-oscillations of the atomic structure of Nd$_2$Fe$_{14}$B nanoclusters

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Abstract. The phenomenon of self-oscillations of the magnetic material atomic structure, occurring at intervals of about 30 days having duration of about 150 days, was observed at the first time. The oscillations are initiated by single field pulse with duration of 1 $\mu$s. The essence of the fluctuations was found due to the redistribution of the iron atoms over the six crystallographic non-equivalent positions. To assess the role of vacancies and boron atoms in the oscillations the vibration spectrum of substance has been calculated.

1. Introduction

The collective synergetic behavior of atoms and molecules in condensed media was discovered long ago and continues to be studied today. The place and role of Mössbauer spectroscopy in this area are still not sharply defined. The unique possibilities of the nuclear gamma-resonance phenomenon are either little-known or virtually unknown. This work is devoted to considering some aspects of the above problem.

The self-organization and self-oscillation concerns a very vast class of phenomena of quite different nature. The phenomenon of self-oscillations in liquids was observed in a reaction with periodic (over several minutes) color changes [1]. Oxidation took place in a malonic acid solution with the presence of cerium sulphate and potassium bromate. The color change (from red to blue) was due to fluctuating changes in the cerium ion valence. The reaction was also accompanied by the appearance of spatial ordering in the system (concentric waves on the liquid’s surface). The first researchers of this reaction were amazed the synchronism of molecular behavior in macroscopic volumes of the matter.

Another typical example is so-called Benar cells in a layer of oil heated on a planar surface [2]. Hexagonal cells of $\sim 10^{-1}$ cm shape the liquid’s surface into a stable spatial structure. The liquid flows in neighboring cells are directed oppositely one another.

We should note that periodic reactions in chemistry are observed quite often, but such processes rarely occur in a solid body. This is apparently connected with the sharp difference between atom mobilities in liquids and solid bodies. Diffusion in crystals and amorphous bodies is a slow process. Weeks, months, and even years are sometimes required to notice any periodicity. The question therefore arises: which method from the arsenal of experimental physics is better suited to this
problem? It is evident that nuclear $\gamma$-resonance is an extraordinarily appropriate and promising method in this case.

2. Experimental
An object for the synergetic phenomenon study was carefully chosen. According to the previous research experience [3] the following requirements were taken into account.

1. It had to be a metallic one with a large number of atoms per unit cell and with multiple pathways for the atoms migration in the crystal.

2. The crystal should possess both stoichiometric vacancies, which ensure high migration speed, and light atoms, which can be the initiators of self-organization process.

3. The initial magnetic structure of the crystal had to be rather simple, allowing properly assess the form of its deformation in fluctuation process.

4. It had to be energy intensive structure, ensuring the creation of a long living non-equilibrium state due to external influence (electric or magnetic). Energy intensity is associated with high values of magnetic and magnetoelastic energy.

Nd$_2$Fe$_{14}$B crystal meets all of these requirements. Its crystalline structure is shown in figure 1.

![Figure 1. Crystalline structure of Nd$_2$Fe$_{14}$B compound.](image)

This is a tetragonal structure ($a = 8.8$ Å and $c = 12.19$ Å), including 68 atoms per unit cell [4]. There are six crystallographically nonequivalent Fe atom positions: $16k_1$, $16k_2$, $8j_1$, $8j_2$ and $4e$ and $4c$; two nonequivalent Nd atom positions; and one position of B atoms. Its magnetic structure at $T = 293K$.
is quite simple: it is a collinear ferromagnetic. Nd$_2$Fe$_{14}$B compound is used in the fabrication of permanent magnets with record high magnetic energy of ~35 MGs Oe. Its magnetic anisotropy is ~10$^7$ erg cm$^{-3}$, and its magnetostriction constant is ~10$^{-3}$. Our sample, prepared by the agglomeration method, contained a certain number of stoichiometric vacancies (~2 vacancies per one unit cell).

The sample was activated using the method traditionally applied in earlier experiments: an electric pulse, $dE/dt \approx 10^8$ kV cm$^{-1}$ s$^{-1}$, emitted when the plates of the capacitor containing the sample were closed. A $^{57}$Co source in Pd was used. A selection of different models was employed in spectrum processing: a model of a continuous distribution of hyperfine fields $p(H)$; calculations of the density function of probability distribution $\rho(V)$ for resonance line centers of gravity according to a scale of rates; and a model of discrete distribution by four, five, and six sextets. A four-sextet model with variable parameters of hyperfine field $H_{hf}$, isomeric shift $\delta$, quadrupole splitting $Q$, line width $\Gamma$, and relative weight $A$ of a partial sextet turned out to be the best suited to our purpose, and the most reliable one. Typical processing parameters are shown in the Table 1. Mössbauer spectra were analyzed by “Univem” program.

| Sextet | $H_{hf}$, kOe | $A$, % | $\delta$, mm/s | $Q$, mm/s | $\Gamma$, mm/s |
|--------|---------------|-------|----------------|-----------|----------------|
| 1      | 333 – $H_1$   | 10    | 0.45           | -0.16     | 0.5            |
| 2      | 290 – $H_2$   | 30    | -0.33          | -0.02     | 0.5            |
| 3      | 285 – $H_3$   | 40    | -0.16          | 0.41      | 0.5            |
| 4      | 250 – $H_4$   | 20    | -0.17          | 0.08      | 0.5            |

On the basis of the known data [5], it was established that field $H_1$ corresponded to the position $j_2$; $H_2$ corresponded to the position $k_2$; and $H_4$ corresponded to the position $c$. Field $H_3$ corresponded to the sum of positions ($k_1 + j_1 + e$), which differ only slightly in their parameters of hyperfine interactions. In our study the behaviour of parameters $A_2$ and $A_3$ (i.e., the behaviour of the occupancies of positions $k_2$ and ($k_1 + j_1 + e$)) was the most interesting. Average values of parameters $A_2$ and $A_3$ are about 30% and 40%, respectively. About 10% and 20% corresponds to positions $j_2$ and positions $c$. These values are calculated from the spectra in accordance with partial weights of Zeeman’s sextets with different $H_{hf}$ values.

3. Results and discussion

The behaviour of an activated sample exhibits the emergence of a clear time order. It was found that strong fluctuation processes are observed in parameters $H_2$, $H_3$, $\delta_2$, $\delta_3$, $A_2$, and $A_3$ (i.e., in the second and third sextets). Figure 2 shows the time dependence of parameters $A_2$ and $A_3$. Explicit fluctuations with a period of ~30 days and a lifetime of ~150 days are observed. Amplitude $\Delta = A_3 - A_2$ is very large: ~5% to ~20%. The places where the curves converge and intersect may be labeled inversion points, since here $A_2 \geq A_3$. The lower curve in figure 2 is an internal reference point, as it shows the stability in the occupancies $A_1$ of the $j_2$ positions. Fluctuations in parameters $\Delta H = H_2 - H_1$ and $\Delta \delta = \delta_2 - \delta_3$ were also observed. These fluctuations were quite regular as well, but had a period of 8–12 days and a concurrent antiphase (i.e., a reduction in $\Delta H$ corresponds to an increase in $\Delta \delta$). Let us now consider the microscopic mechanism of the observed phenomenon.

For this purpose we calculated the Nd$_2$Fe$_{14}$B infrared spectrum. The X-ray data [4] was used for the initial spatial structure of Nd$_2$Fe$_{14}$B. The structure was optimized by molecular mechanics force field MM2 [6]. The optimization was fulfilled with well-known Polak-Rebiery approach with RMS gradient value limit 0.001 kcal/unit. The optimized structure was used for the calculation of the vibration spectrum represented in figure 3a. The calculation of the vibration spectrum and the normal coordinate analysis were performed within approximation of the valence force field. The basis of this
approach is the fact that Fourier transform of velocity autocorrelation function defines the density of vibration states. In the proposed work an analytical expression of the autocorrelation function and its Fourier transform have been found in approach of the cyclic boundary conditions. The curve of the Fourier transform includes a number of sharp peaks, whose positions define the frequency of the normal vibration modes and their areas correspond to the masses that are vibrating with these modes.

Then, one of $8/3$ iron atoms was removed from the original unit cell and the same sequence of calculations was repeated. The resulting spectrum is shown in figure 3b.

![Figure 2](image.png)

**Figure 2.** The time dependence of $A$ parameters of Nd$_2$Fe$_{14}$B compound perturbed by an electrical impact: (a) $A_3$, (b) $A_2$, (c) $A_1$.

![Figure 3](image.png)

**Figure 3.** Calculated IR spectra of (a) Nd$_2$Fe$_{14}$B and (b) Nd$_2$Fe$_{13.75}$B compounds.

The spectra have significant difference, both in position and quantity of the bands. The lowest frequencies of the vibration spectra correspond to boron atoms and to the ensemble of boron and the surrounding iron atoms.
We can conclude that:
1. The presence of stoichiometric vacancies has the influence on the vibration bands. In the low frequency part of spectrum Fig.3b bands of vibration combines in regions of the discontinuous spectrum.
2. It means that the energy difference between atoms in different positions is not great. For example, \( k_2 \) easily transferred to \( (k_1 + j_1 + e) \). It is sufficiently to slightly change the distance between atoms and bond angles, which is provided by electron impact.
3 Moving the light atoms of B between vacancies distributes wave of transformations \( k_2 \rightarrow (k_1 + j_1 + e) \) on the whole sample. This is the reason of the macroscopic time needed for the process.

Synchronic movement of atoms between vacant positions in the whole volume of the sample occurs, by all means, for the following reasons.
1. One start time for the whole sample - the time of electric shock.
2. Mutual influence of cells on each other by electrical and magnetic exchange interaction.

The duration of the process of moving atoms (it takes several days) is obviously due to diffusive nature of the process. The energy barrier for this type movement is at about 1 eV.

Filling of vacant positions \( j_2 \) within 15 days causes a change in the whole crystal structure of the substance, which becomes high energetic, and then slowly relaxes to its original state (figure 2). However, the magnetoelastic interaction energy of the sample, which was increased due to the electric shock, is not being spent completely. This causes a second round of oscillation caused by internal rather than external reasons. After the 5th round the energy is completely spent and the oscillation process breaks down.

4. Conclusions

Self-oscillations of the local atomic structure of the Nd\(_2\)Fe\(_{14}\)B crystal were observed by Mössbauer spectroscopy. Calculations by molecular mechanics method suggest the mechanism of the phenomenon, based on filling the vacant position by moving of boron atoms.

References
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