Journal of ELECTRICAL ENGINEERING, VOL. 62, NO. 4, 2011, 239–243

HOPKINSON EFFECT STUDY IN SPINEL AND HEXAGONAL FERRITES

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The magnetic susceptibility shows a Hopkinson peak just below the Curie temperature T_C when heating the selected hexagonal and spinel ferrite samples. It is proposed that this peak can be associated with a transition from stable magnetic state to super-paramagnetic relaxation above the blocking temperature up to the T_C. The Hopkinson effect results are compared with SEM micrographs of both studied hexagonal and spinel ferrites.

K e y w o r d s: Hopkinson effect, super-paramagnetic relaxation, blocking temperature, spinel and hexagonal ferrite

1 INTRODUCTION

Some susceptibility temperature dependences $\chi(T)$ show a peak just below the Curie temperature T_C when heating the sample, *ie* the Hopkinson effect [1].

The accepted explanation of the Hopkinson effect is based only on domain-wall motion. Due to heating soft magnetic sample the domain-wall mobility increases and consequently the magnetic susceptibility increases as well. This idea is obviously inapplicable to the case of single-domain particles [2–5]. We observed however the Hopkinson effect in many $\chi(T)$ dependences of the hexagonal (Ba, Sr) ferrite samples, or in (not only single domain) particle ferrite samples. We investigated the Hopkinson effect in ferrites both with the spinel structure, as well as with hexagonal structure. The explanation of experimentally observed Hopkinson peak based on super-paramagnetic state at a blocking temperature T_B just below T_C is proposed. This peak turns out to be associated with the transition from the region of stable magnetization to super-paramagnetic state with connection of drastic fall of magnetic anisotropy.

In the present work we discuss fluctuations of magnetization above T_B in particles with magnetic energy, and the influence of these fluctuations on the magnetic susceptibility.

2 OVERVIEW OF THE SUPER–PARAMAGNETIC RELAXATION

It is known that sphere particle is expected to be composed of a single domain at critical radius

$$D_S = 9A_W/M_S^2\,, \tag{1}$$

where A_W is domain wall energy. As example the critical single domain size for spherical isolated particles has been predicted to be 0.5μm [2] for Ba ferrite and nearly 1 μm for NiZn ferrite at room temperature.

For a particle with a volume V and with uniaxial symmetry, the anisotropy energy can be written in the form $A(\theta) = KV\sin^2\theta$. Assume an assembly of uniaxial particles with their easy axes mutually parallel. Let the assembly be initially saturated in one easy direction. A field H is then applied in the oposite direction, so that M_S ineach particles makes an angle θ with easy direction. The total energy per particle is then

$$A(\theta) = V(K\sin^2\theta + HM_S\cos\theta)\,. \tag{2}$$

In the single domain particle assemblies theory it is assumed that the homogeneous rotation of magnetization takes place, *ie* the magnetic moments of the individual atoms remains parallel during the rotation. As the particle size decreases below D_S the anisotropy (effective anisotropy field H_a) and H_C decreases, because of thermal effects. For particles which are lower than a certain critical size D_p (of mono-domain particle), the magnetization may be non-uniform during the transitions between easy directions, and then the super-paramagnetic relaxation takes place via several modes (the homogeneous rotation, the curling or the fanning). Néel found that the super-paramagnetic relaxation time τ is given by an expression of the type

$$\tau = \tau_0 \exp(KV/kT)\,, \tag{3}$$

where τ_0 is of the order of 10^{-9}–10^{-12}s s and it slightly depends on the temperature T, k is Boltzmann constant. Because τ varies very rapidly with V (3), thus it is possible to define, an upper limit volume V_p (or D_p) for

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DOI: 10.2478/v10187-011-0038-7, ISSN 1335-3632

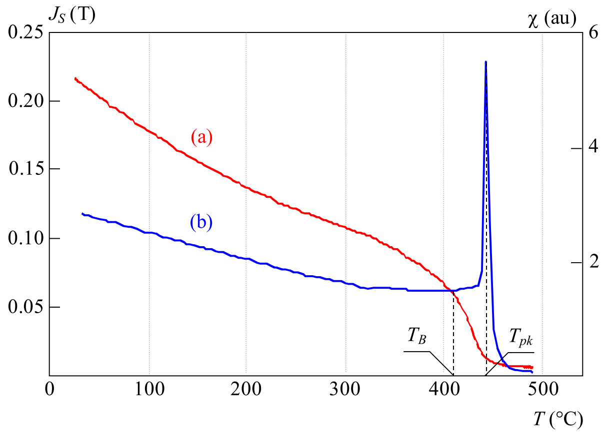

Fig. 1. Temperature dependences of the saturation $J_S(T)$ (a) and initial susceptibility $\chi(T)$ (b) of strontium ferrite

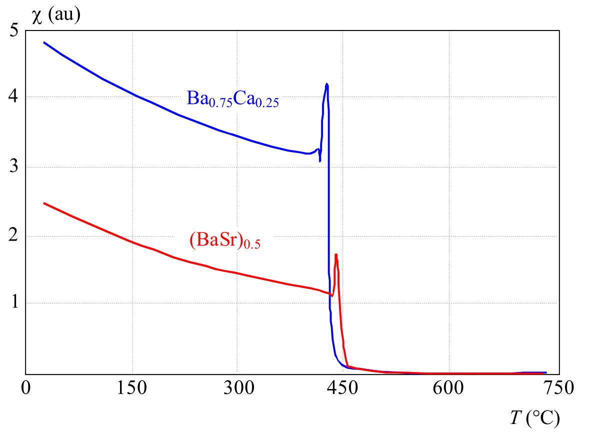

Fig. 2. Temperature dependence of the magnetic susceptibility $\chi(T)$ of substituted $Ba_{0.75}Ca_{0.25}$ and $(BaSr)_{0.5}$ samples

super-paramagnetic behavior by rather arbitrarily letting the value of τ equal to 100 sec mark the transition to stable behavior. With this value of τ, the exponent KV_p/kT of Boltzmann factor becomes equal to 25. The transition to stable behaviour occurs therefore when the energy barrier becomes equal to $25\,kT$. For uniaxial particles,

$$V_p = \frac{25kT}{K} \tag{4}$$

and the corresponding diameter (or size) D_p can be calculated for any given particle shape [6]. It is a value which marks the upper limit of super-paramagnetic state, and the term unstable refers to particles which have relaxation times shorter than 100 sec. The term stable refers to particles which have relaxation times longer than 100 sec. For single domain particle the $K = H_a M_S/2$ and then the critical volume for super-paramagnetic particles is also given by

$$V_p = \frac{50kT}{M_s H_a}\,. \tag{5}$$

For particles of constant size there exists a temperature T_B, called the blocking temperature, below which the magnetization is stable. For uniaxial particles and the same criterion of stability

$$T_B = \frac{KV_p}{25k}\,. \tag{6}$$

The blocking temperature T_B of small magnetic particle is defined as the temperature below which the super-paramagnetic relaxation is negligible. It is the relaxation of M among the easy directions can be considered negligible. Well below the blocking temperature the magnetization vector remains directed close to an easy axis direction. In magnetic measurements T_B is also defined as the temperature at super-paramagnetic relaxation time $\tau_P = 100$ sec.

3 EXPLANATION OF THE HOPKINSON EFFECT IN HEXAGONAL FERRITES

In the paper, the temperature dependences of the magnetic susceptibility $\chi(T)$ and T_C were determined by the bridge method in an alternating magnetic field of 421 A/m at 920 Hz [5]. The susceptibility data of all (particle assembly) samples were determined from the initial susceptibility. The measured temperature dependence of susceptibility curve of $SrFe_{12}O_{19}$ hexaferrite (particles) sample is shown in Fig. 1. The measured $\chi(T)$ curve of $BaFe_{12}O_{19}$ hexaferrite (particles) sample had qualitatively the same behaviour. The Sr and Ba ferrites were prepared by combustion synthesis at 750 °C/3h. The $\chi(T)$ of both ferrites have well defined peak just below the T_C.

The shape of the thermo-magnetic curve shows the characteristic peculiarities of the Hopkinson effect. The susceptibility $\chi(T)$ can be expressed by the formula

$$\chi = \frac{J_S^2}{A_{\text{eff}}} \approx \frac{J_S}{H_a}\,. \tag{7}$$

It appears as consequence of super-paramagnetism in particles at $T > T_B$, we assume.

Starting from the room temperature, $\chi(T)$ decreases mainly due to the decrease of saturation polarization J_S up to $T = T_B$, as can be shown. All particles are magnetically stable (blocked) at temperature $T < T_B$. At the blocking temperature $T_B \sim 410$ °C this decreasing changes to a strong increase starting in a local minimum of $\chi(T)$ due to $J_S(T)/H_a(T)$ increasing, although both J_S and H_a still decrease. Probably at the temperature T_B the content of super-paramagnetic particles increase in our case. The approach to Hopkinson peak in $\chi(T)$ behaviours of particle assemblies can take into account super-paramagnetic state of particles above the blocking temperature T_B.

Hopkinson peak is at the temperature $T_{Pk} \sim 440$ °C. At this temperature, major part of particles is super-paramagnetic and H_a approaches zero, so the amplitude of the Hopkinson peak is several times larger than the value of $\chi(T)$ at the local minimum at T_B. The H_a (or KV_P) become so small that energy fluctuations could

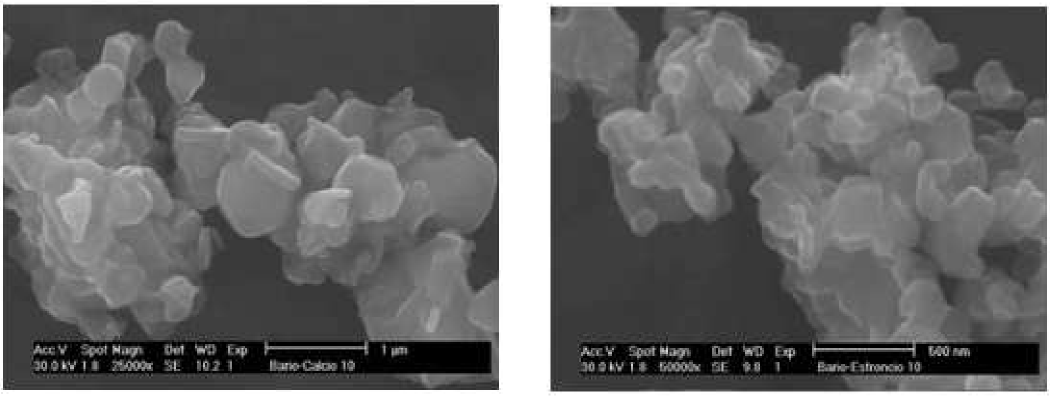

Fig. 3. SEM micrographs of synthesized mixtures. a. $Ba_{0.75}Ca_{0.25}$ b. $(BaSr)_{0.5}$

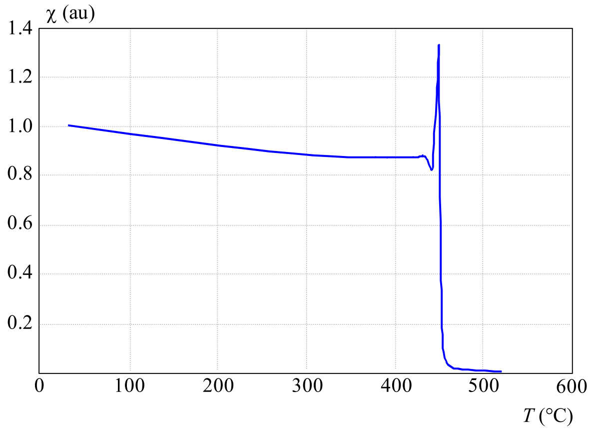

Fig. 4. Temperature dependence of the initial magnetic susceptibility $\chi(T)$ of sintered strontium ferite ball sample

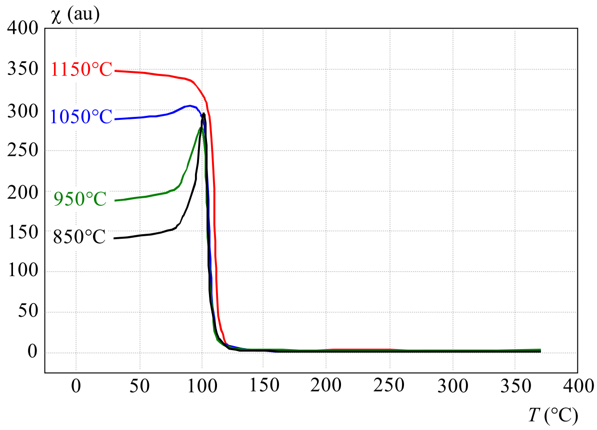

Fig. 5. Temperature dependences of the initial susceptibility $\chi(T)$ of $Ni_{0.33}Zn_{0.67}Fe_2O_4$ ferrite samples annealed at 850 °C, 950 °C, 1050 °C and 1150 °C

overcome the anisotropy forces and spontaneously reverse the magnetization of a particles from one easy direction to the other, even in the absence of applied field. Thus the super-paramagnetic relaxation is reason that the decrease of the anisotropy forces of particles is faster than the magnetization fluctuations. Due to that, the main reason of the emergence of Hopkinson peak is a rapid decrease of $H_a(T)$, when $V_P \to V$ as follows

$$H_a = H_{a0}\Big[1 - \Big(\frac{V_p(T)}{V}\Big)^{1/2}\Big]. \tag{8}$$

Here H_{a0} is the anisotropy field when field is unaided by thermal energy. The H_a therefore decreases as the particle volume V (or D) decreases to V_P (or D_P). For a particle with a magnetic energy given by $KV\sin^2\theta$, and with the magnetization vector fluctuating around the easy direction at $\theta = 0$, and with the probability that the magnetization vector forms an angle between θ and $\theta + \mathrm{d}\theta$ with the easy direction, the average magnetization at $T > T_B$ is given by [7]

$$M(V) = M(V = V_p, T)\langle\cos\theta\rangle_T \tag{9}$$

where

$$\langle\cos\theta\rangle_T = \frac{\int_0^{\pi/2}\exp\{-A(\theta)/kT\}\cos\theta\sin\theta\mathrm{d}\theta}{\int_0^{\pi/2}\exp\{-A(\theta)/kT\}\sin\theta\mathrm{d}\theta}.$$

This term together with (8) can be accepted in the (7) instead of J_S/μ_0 for temperature at $T > T_B$. At the Curie temperature $T_C \sim 450$ °C, the susceptibility strongly decreases to zero because spontaneous polarisation (magnetization) vanishes, J_S $(M_S) \to 0$ and the system becomes to be a normal paramagnet.

Figure 2 shows another measured temperature dependences of the magnetic susceptibility, $\chi(T)$ for substituted $Ba_{0.75}Ca_{0.25}$ and $(BaSr)_{0.5}$ hexaferrite samples. The samples were prepared by mechanical alloying at 1050 °C/1.5 h. Figure 3 shows SEM micrographs of both studied mixtures. All particles have nearly hexagonal-platelet shape. The $Ba_{0.75}Ca_{0.25}$ powders look with round corners and average particle size larger than that of $(BaSr)_{0.5}$ mixture. Therefore the value of χ at room temperature for $Ba_{0.75}Ca_{0.25}$ are higher (approximately twice) that as for $(BaSr)_{0.5}$ (see Fig. 2), because the initial susceptibility is proportional to D. However, it is clear that the particle size is much below 1 μm (or 0.5 μm for $(BaSr)_{0.5}$), thus a part of particles size is below D_P and they are magnetically unstable at temperature $T > T_B$. Due to super-paramagnetic relaxation behaviour of both thermo-magnetic curves these show the characteristic peculiarities of the Hopkinson effect.

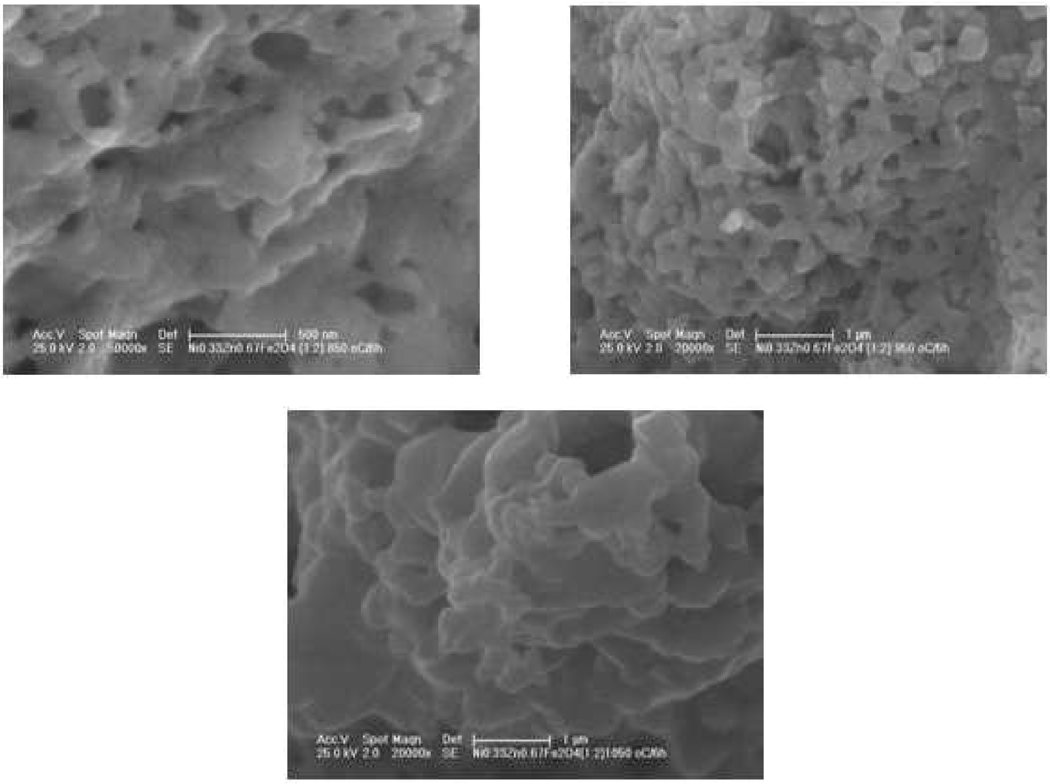

Fig. 6. SEM micrographs of Ni0.33Zn0.67Fe2O4 ferrite samples annealed at 850 °C, 950 °C and 1050 °C/6 h

Table 1. Magnetic properties and Curie temperature for BaCa and BaSr

0.75Ba0.25Ca $Fe_{12}O_{19}$			
M_s (Am^2/kg)	H_{ci} (kA/m)	M_r (Am^2/kg)	T_c (°C)
59.2	289.6	32.8	440
0.5Ba0.5Sr $Fe_{12}O_{19}$			
M_s (Am^2/kg)	H_{ci} (kA/m)	M_r (Am^2/kg)	T_c (°C)
64.4	389.9	36.3	452

The magnetic properties with the Curie temperature are given in Table 1. It can be observed that the saturation magnetization for $(BaSr)_{0.5}$ sample was higher than that for $Ba_{0.75}Ca_{0.25}$. It was also shown that the intrinsic coercivity is higher for $(BaSr)_{0.5}$ with comparison to $Ba_{0.75}Ca_{0.25}$ sample. It is due to that coercivity tends to decrease according to the well known $1/D$ low.

Figure 4 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ of sintered strontium ferrite sample of the ball shape. The sample was prepared ceramic method at 1250 °C/3h. In this bulk sample the behaviour of the thermo-magnetic curve shows again the characteristic peculiarities of the Hopkinson effect. The contribution of the demagnetizing field to χ is lower in grains of bulk sample which consists of several domains, in comparison with single-domain particle sample. In spite of that, we suppose that this peak can be associated with the transition from the region of stable state to superparamagnetic state of mayor parts of single domain grains in sintered sample.

4 EXPLANATION OF THE HOPKINSON EFFECT OF SPINEL FERRITES

NiZn ferrite samples were prepared from a gellatineous substance by a low-temperature auto-combustion. The Hopkinson effect on the magnetic susceptibility behaviour of NiZn ferrite has been investigated for compositions given by the formula of $(Ni_{0.33}Zn_{0.67})Fe_2O_4$.

As an example, the four temperature dependences of magnetic susceptibility $\chi(T)$ of the samples annealed at temperatures increasing in linear steps of 100 °C are shown in Fig. 5. The curves of the compared samples show that the Curie temperature is the same (samples have identical chemical composition). Figure 6 shows SEM micrographs of three samples synthesized at annealed temperatures 850 °C, 950 °C and 1150 °C. The powders at T_a = 1150 °C have largest average particle size. From both figures one can conclude.

In the first, it can be observed, that at room temperature the susceptibility χ increases with annealing temperature T_a, and the samples with higher grain-size have higher χ value. It is in consequence of that the particles size arises with T_a and the samples with higher particles size have higher χ value again according to D-law.

In the second, one can observed, that all four samples have the same intrinsic properties (T_C and M_S), but they have different dependences of $\chi(T)$. It can be the consequence of that the samples contain particles with different volumes. Therefore, they have disparate values of KV weighted with the particle size distribution of the samples. The existence of the Hopkinson effects is indicated in both samples annealed at $T_a = 850\,°C$ and $950\,°C$. For both these cases the corresponding particle diameters D can be estimated lower as the upper limit D_P of super-paramagnetic state, and they are unstable at $T > T_B \cong 65\,°C$. The main reason of the emergence of Hopkinson peak is again a rapid decrease of $H_a(T)$, when $V_P \to V$ as follows of (8).

The anisotropy of the demagnetization field A_d is in this case zero (or almost zero), since the particles are in super-paramagnetic state. The high value of χ_{Pk} refers to a large number of unstable particles (grains) which are at the temperature of $T \in \langle T_B, T_C \rangle$ in a super-paramagnetic state.

On the other hand, for the sample annealed at $1050\,°C$ corresponding particles diameter D can be estimated as roughly stable diameter, referring to particles which have relaxation times longer than 100 sec. These blocked particles are sufficiently large ($D > D_P$) so that the anisotropy energy barrier cannot be overcome by thermal fluctuations and the magnetization is stable. In the sample annealed at $1150\,°C$ the all particles are larger than the critical diameter D_p, and the magnetization may be uniform during the transitions among the easy directions up to T_C.

5 CONCLUSION

The existence of the Hopkinson effect in a system of single- domain particles of Sr-, $(BaSr)_{0.5}$-, $Ba_{0.75}Ca_{0.25}$-hexaferrites and in a system of NiZn ferrite particles has been experimentally confirmed. The experimentally observed thermomagnetic curves can be explained qualitatively with the help of an approach developed for the super-paramagnetic relaxation. The main feature of the system is a Hopkinson peak of the susceptibility near T_C when heating, the origin of which is the transition from blocked to super-paramagnetic particles. Hopkinson peak appears always close to T_C even for rather different sizes of the particles. It is because there are several materials with different value of T_C, M_S (or J_S) and different value domain wall energy A_W. Then they have disparate value of D_S of mono-domain particles, from that follows different value of their critical diameter D_p. The key to understand the role of Hopkinson peak in particle samples is to recognize that particle (grain) size is smaller than the critical diameter at blocking temperature with the transition from the region of stable state to super-paramagnetic state. The marked dependence of the magnetic properties of very fine particles on their size means that particle sizes can be measured magnetically, by $\chi(T)$ behaviour as example.

Acknowledgement

This work was supported by Scientific Grant Agency of the Ministry of Education of Slovak Republic, No VEGA-1/0575/09 and VEGA-1/0529/10.

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Received 9 January 2011

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