Two-Level Model Description of Superparamagnetic Relaxation in Nanoferrites (Co,Zn)Fe₂O₄

B.F. Bogacz[a,*], R. Gargula[a], P. Kurzydło[a], A.T. Pędziwiatr[a], T. Tatarchuk[b]
and N. Paliychuk[b]

[a]M. Smoluchowski Institute of Physics, Jagiellonian University, S. Łojasiewicza 11, 30-348 Kraków, Poland
[b] Educational and Scientific Center of Material Science and Nanotechnology,
Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, 76018, Ukraine

The process of superparamagnetic relaxation of ferrite nanoparticles (Co,Zn)Fe₂O₄ was observed with the Mössbauer spectroscopy (80–773 K) and described by a two-level relaxation model. Simultaneous fitting of the Mössbauer spectra for a wide range of temperatures enabled a clear evaluation of the theoretical model and also determination of the relaxation rate for each temperature. The analysis of temperature dependence of relaxation rate allowed to estimate an anisotropy constant for the studied ferrite.
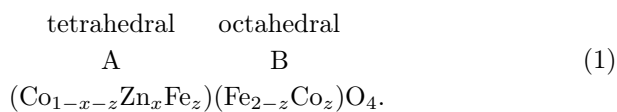
1. Introduction

Nanoparticle ferrites form a group of innovative materials with wide prospects for applications [1–3]. Due to nanosize of particles they exhibit a variety of properties which are different from those observed for bulk form [4–9]. One of these specific properties is superparamagnetism. For small enough particles thermal energy is sufficient to change the direction of the resultant magnetic moment of a particle. Due to strong sensitivity to magnetic fluctuations, the Mössbauer spectroscopy is a suitable technique to observe and investigate such effect. Observation time of this technique (10^{-7} s) is comparable with relaxation time in many compounds in accessible temperature range. In this study the Mössbauer spectroscopy was used to investigate superparamagnetic relaxation phenomenon in nanoferrites (Co,Zn)Fe₂O₄.

Ferrites form a spinel structure described by the general formula AB₂O₄ [10–13] in which metal ions (including Fe) reside in two sublattices: A sublattice in tetrahedral oxygen neighbourhood and B sublattice in octahedral surrounding (Eq. (1)):

$$\text{tetrahedral} \quad \text{octahedral}$$
$$\text{A} \qquad\qquad \text{B}$$
$$(\text{Co}_{1-x-z}\text{Zn}_x\text{Fe}_z)(\text{Fe}_{2-z}\text{Co}_z)\text{O}_4. \tag{1}$$

Because Fe atoms most strongly interact with ions from a counterpart sublattice, the largest influence on magnetic behaviour of Fe atoms in A sublattice comes from the 12 nearest metal ions from B sublattice and on Fe atoms in B sublattice — from 6 nearest metal ions from A sublattice. It was assumed that both iron and

———————

*corresponding author; e-mail: bogdan.bogacz@if.uj.edu.pl

cobalt magnetic ions give similar contribution to hyperfine parameters of the iron atoms in the neighbouring sublattice. Replacement of magnetic Co or Fe ions with non-magnetic Zn ions causes strong reduction of the hyperfine magnetic field on Fe nuclei which are surrounded by Zn. The Zn atoms show very strong preference to occupy A sublattice [14] so they influence only Fe atoms in B sublattice. Fe atoms in A sublattice do not have Zn atoms as nearest neighbours. There are seven different surroundings of Fe atoms residing in B sublattice, corresponding from 0 to 6 Zn atoms in neighborhoods [15], with contributions determined by binomial distribution (Eq. (2)):

$$P(k) = \binom{n}{k} p_A^k (1 - p_A)^{n-k},$$
$$n = 6, \quad k = 0 \div 6, \tag{2}$$

where $P(k)$ is the probability of finding k Zn atoms in the nearest neighbourhood of Fe atoms from B sublattice, p_A — corresponds to the probability of finding Zn atom in A sublattice, in this case $p_A = x$, see Eq. (1).

In ferrite structure Co occupies preferentially B sublatice [14] forming an inverted spinel. However in nanoferrites it happens that a fraction of Co atoms goes to A sublattice and thus forms a partially inverted spinel. Parameter z (Eq. (1)) contains information on the degree of spinel inversion. In the Mössbauer spectrum it decides on the ratio of contributions of sextets attributed to A and B sublattices.

2. Experimental methods

The samples of $(\text{Co}_{1-x-z}\text{Zn}_x\text{Fe}_z)(\text{Fe}_{2-z}\text{Co}_z)\text{O}_4$ cobalt–zinc nanoferrite have been synthesized by chemical co-precipitation method, as described elsewhere [16]. Samples with $x = 0.2$ and 0.4 were used for the Mössbauer studies of superparamagnetic relaxation. X-ray

diffraction (XRD) analysis, using Cu K_α radiation, confirmed the spinel structure. Scanning electron microscopy was used to estimate the particle size. The Mössbauer spectra were recorded at temperatures from 80 K to 773 K, using a ^{57}Co(Rh) source and a computer driven constant acceleration mode spectrometer. The measurements below room temperature were carried out in a cryostat under helium atmosphere with 100 Pa pressure, those above room temperature in the Mössbauer furnace in vacuum 10 Pa. Velocity scale was calibrated using high purity natural iron foil. Isomer shifts were established with respect to the center of gravity of the room temperature iron Mössbauer spectrum.

3. Results and discussion

The exemplary Mössbauer spectra taken for $Co_{0.8}Zn_{0.2}Fe_2O_4$ at different temperatures are shown in Fig. 1. Significant changes in spectra shape were registered with the increase of temperature. Line broadening is evident and, at sufficiently high temperatures, a collapse of the magnetic hyperfine field to the quadrupole doublet is observed which can be explained as a consequence of superparamagnetic relaxation.

Two-level superparamagnetic relaxation model [5, 17–18] was used to describe the spectra. This model is ideal for describing the particle's magnetic moment which changes its direction to the opposite one infinitely fast but randomly in time, remaining parallel or antiparallel to the easiest magnetisation axis of the particle.

Analytic expression for the absorption cross-section $\sigma(\omega)$ (where ω is a frequency of nuclear radiation) of the Mössbauer line for this model is given by Eq. (3) [5]:

$$\sigma(\omega) = -\frac{\sigma_a \Gamma_0}{2} \sum_\alpha |C_\alpha|^2 \, \mathrm{Im} \frac{\bar{\omega} + \mathrm{i}p}{\bar{\omega}^2 - \omega_\alpha^2 + p^2} \tag{3}$$
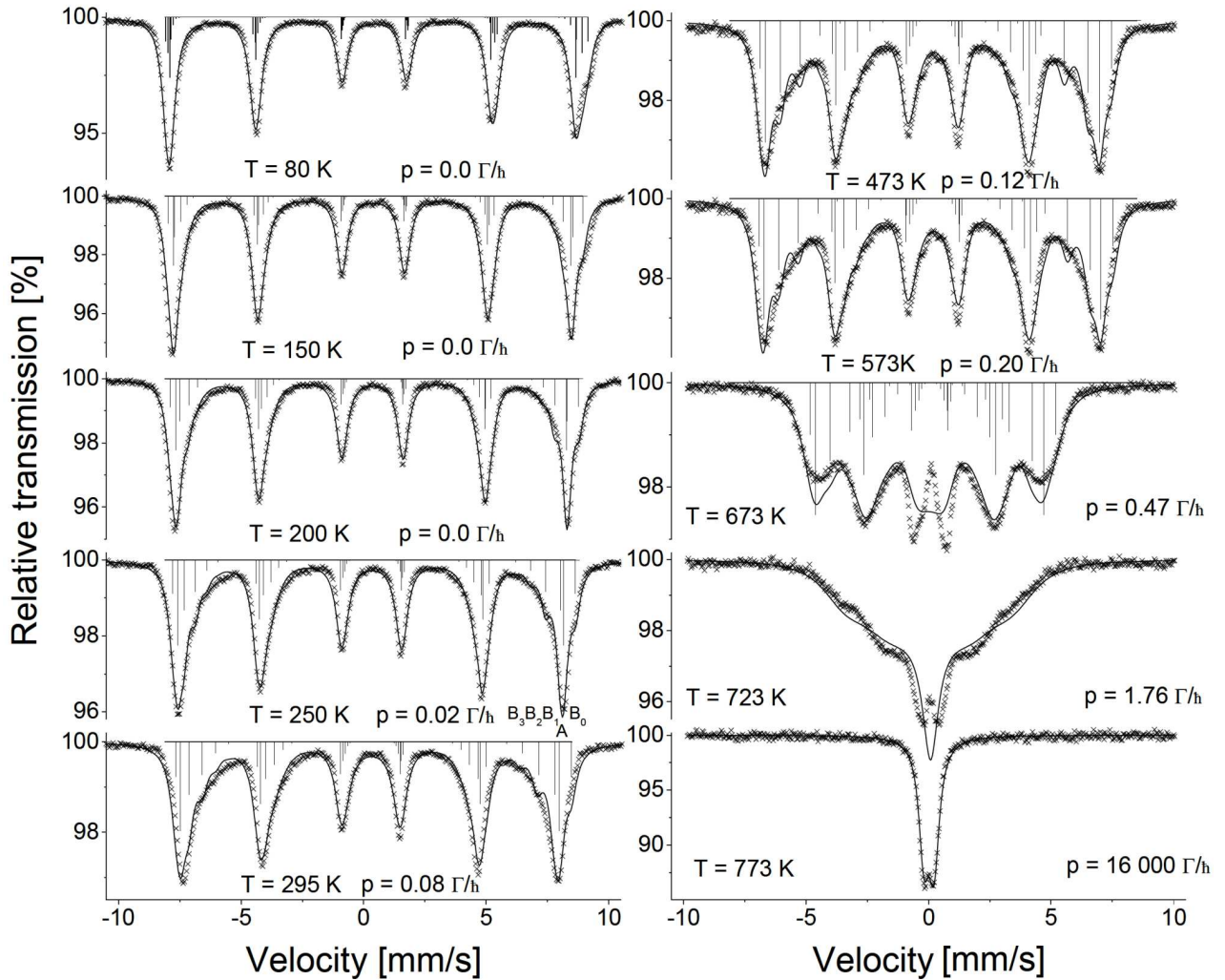

Fig. 1. ^{57}Fe Mössbauer absorption spectra for $Co_{0.8}Zn_{0.2}Fe_2O_4$ ferrite (crosses) described by the two-level relaxation model (solid lines). The stick diagrams show the line positions and their relative intensities. Exemplary positions of lines corresponding to A and B sublattices are marked for 295 K spectrum. The relaxation rate p is indicated for each temperature.

where $\bar{\omega} = \tilde{\omega} + \mathrm{i}\left(\frac{\Gamma_0}{2} + p\right)$, $\tilde{\omega} = \omega - \frac{E_0}{\hbar}$, E_0 is the energy of the resonance transition, σ_a — the effective absorber thickness, Γ_0 — the width of the excited nuclear level. The coefficients C_α are the intensities of the respective transitions. The changing with temperature parameter, relaxation rate p, has the decisive influence on the shape of theoretical spectrum in this model. For low frequencies, $p \ll |\omega_\alpha|$, one gets a well defined magnetically split spectrum. With increase of relaxation frequency the spectrum shape is changing: the lines become broadened and a contribution of inner lines increases. For the fast relaxation limit the spectrum collapses into a single central line or a quadrupole doublet with narrow lines.

The described above two-level relaxation model was applied in simultaneous fitting procedure of the Mössbauer spectra for different temperatures, by CERN minimizing computer procedure MINUIT. For each spectrum, eight Zeeman sextets were assigned: one corresponding to Fe atoms in A sublattice and seven sextets corresponding to Fe atoms in B sublattice, with contributions determined by binomial distribution (Eq. (2), Table I). For the presented composition ($x = 0.2$) only five sextets give a non-negligible contribution to the total spectrum (Fig. 1). Additionally, it was assumed that the Zeeman sextets for B sublattice corresponding to increasing consecutive numbers of Zn atoms in the nearest neighbourhood of Fe atoms, differ by constant values in hyperfine interaction parameters ΔB, ΔIS, ΔQS (changes of hyperfine interaction parameters due to one Co or Fe ion by Zn ion replacement) (Tables I, II). Simultaneous fitting of the spectra for a given sample measured at different temperatures allows to describe these spectra using a common set of parameters connected with horizontal scale; hyperfine interactions and line widths (Table II). Obviously, it is necessary to take into account the change of these parameters with temperature. A linear temperature dependence of

isomer shift, $IS(T)$, and quadrupole splitting, $QS(T)$, with common value of the slope coefficients ΔIST and ΔQST, respectively, for all sextets was assumed. Obtained from fits values of these dependences $\Delta IST = (-0.584 \times 10^{-3} \pm 0.025 \times 10^{-3})$ mm s^{-1} K^{-1} is very close to a theoretical value $(-0.725 \times 10^{-3}$ mm s^{-1} K$^{-1})$ coming from second order Doppler shift.
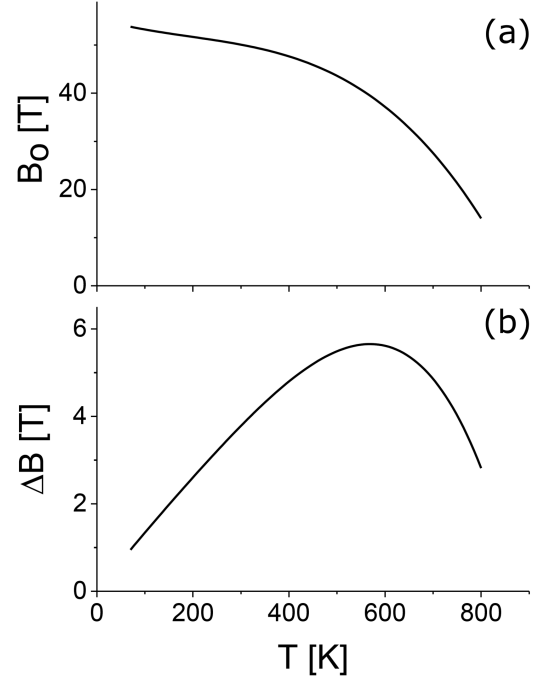

Fig. 2. (a) The temperature dependence of magnetic field $B_0(T)$ (without Zn ions in the nearest neighbourhood) acting on Fe nuclei in B sublattice, (b) the temperature dependence of the change of magnetic field on Fe nuclei in B sublattice $\Delta B(T)$ caused by replacing one magnetic ion by a non-magnetic Zn ion.

TABLE I

Hyperfine interaction parameters (B — hyperfine field, IS — isomer shift, QS — quadrupole splitting) of the Zeeman sextets corresponding to the number k of Zn ions in the nearest neighbourhood of Fe atoms in B sublattice. C denotes the contributions of sextets calculated from binomial distribution (Eq. (2)). The presented values were calculated for $T = 473$ K based on parameters obtained from fit.

k	0	1	2	3	4	5	6
C [%]	26.2	39.3	24.6	8.2	1.5	0.2	0.0
B_k [T] (± 0.5)	44.49	39.00	33.51	28.02	22.53	17.04	11.55
IS_k [mm/s] (± 0.05)	0.26	0.22	0.19	0.15	0.12	0.08	0.04
QS_k [mm/s] (± 0.05)	0.034	-0.002	-0.038	-0.074	-0.110	-0.146	-0.182

TABLE II

Fitted parameters related to the horizontal scale of the Mössbauer spectra. SL — sublattices, B — magnetic field, IS — isomer shift, QS — quadrupole splitting, ΔB, ΔIS, ΔQS — changes of hyperfine interaction parameters due to one magnetic ion replacement by Zn ion, Γ — the Zeeman line widths. All values correspond to 473 K temperature.

SL	B [T] (± 0.5)	IS [mm/s] (± 0.02)	QS [mm/s] (± 0.02)	ΔB [T] (± 0.5)	ΔIS [mm/s] (± 0.01)	ΔQS [mm/s] (± 0.01)	Γ_1 [mm/s] (± 0.01)	Γ_2 [mm/s] (± 0.01)	Γ_3 [mm/s] (± 0.01)
A	42.31	0.16	-0.005	–	–	–			
A, B							0.426	0.468	0.496
B	44.49	0.26	0.034	-5.49	-0.036	-0.036			

The values of the Mössbauer hyperfine interaction parameters of $Co_{0.8}Zn_{0.2}Fe_2O_4$ calculated, for given temperature, based on the fitted temperature dependences, B — hyperfine field, IS — isomer shift, QS — quadrupole splitting. Hyperfine field for sublattice B corresponds to zero Zn ions in the nearest neighbourhood of Fe atom. ΔB — change of magnetic field caused by a replacement of one magnetic ion by Zn ion in the nearest neighbourhood of Fe ion in B sublattice. p is the relaxation rate obtained from fits.

| T [K]	Sublattice	B [T] (± 0.5)	IS [mm/s] (± 0.02)	QS [mm/s] (± 0.02)	ΔB [T] (± 0.5)	p [$\Gamma/\hbar$] (± 0.1)
80	A	51.26	0.39	−0.011		0.00
	B	53.45	0.49	0.027	−1.11	
150	A	50.36	0.35	−0.011		0.00
	B	52.55	0.45	0.029	−2.06	
200	A	49.67	0.32	-0.010		0.00
	B	51.86	0.42	0.029	−2.67	
250	A	48.87	0.29	−0.009		0.02
	B	51.06	0.39	0.030	−3.33	
295	A	48.00	0.26	−0.008		0.08
	B	50.19	0.36	0.031	−3.86	
473	A	42.31	0.16	−0.005		0.12
	B	44.49	0.26	0.034	−5.49	
573	A	36.77	0.10	−0.003		0.20
	B	38.95	0.20	0.036	−5.82	
673	A	28.91	0.04	−0.002		0.47
	B	31.10	0.14	0.038	−5.46	
723	A	23.96	0.01	−0.001		1.76
	B	26.14	0.11	0.038	−4.93	
773	A	18.24	−0.01	0.000		16000
	B	20.42	0.09	0.039	−4.12	
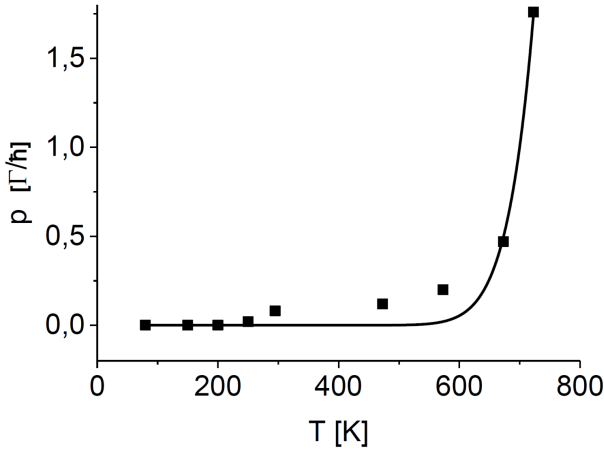
Fig. 3. Temperature dependence of the relaxation rate (black squares) obtained from the description of experimental spectra by two-level relaxation model. Solid line presents theoretical dependence given by the Arrhenius law.

A value for quadrupole splitting $\Delta QST = (0.017 \times 10^{-3} \pm 0.048 \times 10^{-3})$ mm s^{-1} K^{-1} indicates a very weak temperature dependence of quadrupole splitting. The temperature dependence of the magnetic field, $B(T)$, was described with a third order polynomial (Fig. 2a), with common, excluding the zeroth, coefficients for all sextets. It was assumed that the change of the magnetic field, ΔB at Fe nuclei in B sublattice, caused by a re-

placement of the magnetic ion in the nearest neighbourhood by a nonmagnetic Zn ion, is proportional to temperature and to the field value B_0 (without Zn ions in the nearest neighbourhood) (Fig. 2a, Table I) for a given temperature (Fig. 2b, Table III). Such assumption was the simplest way of describing the observed dependences. No temperature dependence of ΔIS, ΔQS was considered. The only independent parameters for each spectrum are: two parameters of the vertical scale (base and amplitude) and the relaxation frequency p, which is characteristic for each spectrum and which we want to determine. Very strict limitation of the number of fitted parameters allowed to test how the applied two-level relaxation model could describe the shape of experimentally observed spectra (Fig. 1). The decisive parameter influencing the shape of the theoretical spectrum is the relaxation rate, p. Values of this parameter obtained for each temperature, as a result of simultaneous fitting of the used model to the set of spectra, are presented in Figs. 1, 3 and in Table III. For temperatures above 673 K the spectrum shape is determined by relaxation effects (the collapse of the magnetic hyperfine field is visible) which is the reason why the values of hyperfine interaction parameters shown in Table III do not correspond directly with the shape of the spectrum.

The temperature dependence of relaxation rate p is described by the Arrhenius law (Eq. (4)):

$$p = p_0 e^{-\frac{KV}{k_B T}}. \tag{4}$$

Here, p_0 is the fluctuation rate, K is the magnetic anisotropy constant, V is the particle volume, T — temperature and k_B is the Boltzmann constant. By fitting this dependence to experimental data (Fig. 3) one can obtain an estimate of K, if particle size is known [19]. For particle size 40 nm an anisotropy constant $K = (5000 \pm 1000)$ J/m^3 was obtained.

4. Conclusions

Using a two-level relaxation model it was possible to describe the character of temperature changes of experimental Mössbauer spectra. The procedure of simultaneous fitting of several spectra for different temperatures allowed to determine the parameters of temperature dependence of hyperfine interaction parameters, and consequently to calculate these parameters for A and B sublattices, for all temperatures (Table III). As a result of fitting, the value of spinel inversion parameter $z = 0.80 \pm 0.02$ (Eq. (1)) was obtained, which indicates that all Co atoms are located in B sublattice. Determination of superparamagnetic relaxation rate for different temperatures allowed to estimate magnetic anisotropy.

Acknowledgments

References

[1] E.S. Murdock, R.F. Simmons, R. Davidson, *IEEE Trans. Magn.* **28**, 3078 (1992).

[2] I.S. Lyubuthin, N.E. Gervits, S.S. Starchikov, Chun-Rong Lin, Yaw-Teng Tseng, Kun-Yauh Shih, Cheng-Chien Wang, I.-Han Chen, Yu.L. Ogarkova, N.Yu. Korotkov, *Smart Mater. Struct.* **25**, 015022 (2016).

[3] F. Hu, K.W. MacRenaris, E.A. Waters, E.A. Schultz-Sikma, A.L. Eckermann, T.J. Meade, *Chem. Commun.* **46**, 73 (2010).

[4] P. Didukh, J.M. Greneche, A. Ślawska- Waniewska, P.C. Fannin, Ll. Casas, *J. Magn. Magn. Mater.* **242-245**, 613 (2002).

[5] M.A. Chuev, *J. Phys. Condens. Matter* **23**, 426003 (2011).

[6] S.W. Lee, C.S. Kim, *J. Magn. Magn. Mater.* **303**, e315 (2006).

[7] E.J. Choi, Y. Ahn, S. Kim, D.H. An, K.U. Kang, B.G. Lee, K.S. Baek, H.N. Oak, *J. Magn. Magn. Mater.* **262**, L198 (2003).

[8] H.N. Oak, K.S. Beak, Y. Jo, *Solid State Commun.* **100**, 467 (1996).

[9] A. Ghasemi, V. Sepelak, S.E. Shirsath, X. Liu, A. Morisako, *J. Appl. Phys.* **109**, 07A512 (2011).

[10] W.H. Bragg, *Philos. Mag.* **30**, 305 (1915).

[11] S. Nishikawa, *Proc. Tokyo Math.-Phys. Soc.* **8**, 199 (1915).

[12] B.R. Babu, T. Tatarchuk, *Mater. Chem. Phys.* **207**, 534 (2018).

[13] T.R. Tatarchuk, N.D. Paliychuk, M. Bououdina, B. Al-Najar, M. Pacia, W. Macyk, A. Shyichuk, *J. Alloys Comp.* **731**, 1256 (2018).

[14] R.C. O'Handley, *Modern Magnetic Materials*, Wiley, New York 2000.

[15] T.A.S. Ferreira, J.C. Waerenborgh, M.H.R.M. Mendonca, M.R. Nunes, F.M. Costa, *J. Solid State Sci.* **5**, 383 (2003).

[16] T.R. Tatarchuk, M. Bououdina, N.D. Paliychuk, I.P. Yaremiy, V.V Moklyak, *J. Alloys Comp.* **694**, 777 (2017).

[17] H.H. Wickman, in: *Mössbauer Effect Methodology*, Vol. 2, Ed. I.J. Gruverman, Plenum, New York 1966.

[18] M. Blume, J.A. Tjon, *Phys. Rev.* **165**, 446 (1968).

[19] R.S. de Biasi, L.H.C. Cardoso, *Physica B* **407**, 3893 (2012).