Reprinted from

journal of magnetism and magnetic materials

Journal of Magnetism and Magnetic Materials 184 (1998) 222–226

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G.N. Abelyashev[a], V.N. Berzhansky[a,*], Yu.V. Fedotov[b], S.N. Polulyakh[a], N.A. Sergeev[c]

[a] *Simferopol State University, Yaltinskaya 4, 333036 Simferopol, Ukraine*
[b] *Institute of Physics, National Academy of Sci., prospekt Nauki 46, 252650 Kiev, Ukraine*
[c] *Szczecin University, 70-451 Szczecin, Poland*

Received 15 July 1997; received in revised form 25 November 1997

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[a] *Simferopol State University, Yaltinskaya 4, 333036 Simferopol, Ukraine*
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Abstract

The decay of spin echo from ^{53}Cr nuclei in ferromagnetic semiconductors $Cd_{1-x}Ag_xCr_2Se_4$ with spinel structures is investigated at the temperature $T = 4.2$ K. The transverse relaxation rate T_2^{-1} is studied in multidomain polycrystalline samples. The dependence of the relaxation rate on the resonance frequency and on the concentration of silver is determined. The transverse relaxation rate is separated into isotropic and anisotropic parts. Directional fluctuations of the magnetization are shown to be the source of the T_2^{-1} anisotropy. The electron exchange between the Cr^{4+} impurity ions with a strong spin–orbit coupling and the valence band is proposed as a possible origin of such fluctuations.

Keywords: Nuclear magnetic resonance; Nuclear magnetic relaxation; Magnetically ordered substances; Ferromagnets

1. Introduction

An important practical application of nuclear magnetic resonance (NMR) in magnetically ordered substances is a study of the dynamic processes in an electron spin system with exchange interactions. The relaxation characteristics of nuclear paramagnetic spin systems are traditionally used for such investigations. The source of the transverse relaxation in paramagnetic spin systems is the longitudinal magnetic field component fluctuations [1,2]. In magnetically ordered substances the presence of hyperfine interactions as well as exchange interactions in electron spin systems results in the appearance of strong magnetic fields on the nuclei [3]. It has been shown that the dynamic processes in electron spin systems can result in direct fluctuations of longitudinal hyperfine field components and cause a transverse magnetic relaxation of nuclear spins [4].

A special case is represented by the nuclei of ions in lattice positions with a noncubic environment. In axial symmetry, the hyperfine field is more or less

* Corresponding author. E-mail: roton@ccssu.crimea.ua.

0304-8853/98/$19.00
PII S0304-8853(97)01137-2

anisotropic, depending on the orbital ground state. The directional fluctuations of the magnetization result in fluctuations of the longitudinal component of the magnetic field on a nucleus. The transverse relaxation caused by such magnetization fluctuations has been investigated in Ref. [5] on ^{57}Fe nuclei which have no electrical quadrupole moment.

In the present work, the transverse magnetic relaxation of the ^{53}Cr nuclei with spin $I = \frac{3}{2}$ in the system of silver–doped ferromagnetic chalcogenide spinels $CdCr_2Se_4$ is investigated. For nuclei with spin $I > \frac{1}{2}$, the magnetization orientation does not only affect the resonance frequency, but also the NMR quadrupole splitting. The influence of orientation fluctuations on the nuclear transverse magnetic relaxation is taken into account within the framework of the spectral diffusion model proposed for nonzero quadrupole nuclei in Ref. [6]. Only the component of transverse relaxation rate which depends on frequency is analyzed.

2. Experimental results and discussion

The experiments have been carried out, at 4.2 K on ferromagnetic polycrystalline samples of $Cd_{1-x}Ag_xCr_2Se_4$ with $x = 0$, 0.001, 0.005, 0.015, and 0.030. A broadband incoherent pulse NMR spectrometer has been used for the study of ^{53}Cr spin-echo signals.

The investigated samples have the spinel structure, in which cadmium and silver ions occupy tetrahedral (A) sites. The chromium ions occupying octahedral (B) sites are responsible for the ferromagnetic ordering. The local symmetry of the octahedral sites is trigonal. The axis of symmetry coincides with one of the $\langle 1\,1\,1\rangle$ lattice directions of the cubic spinel structure, resulting in four magnetically nonequivalent sites.

The nuclei of ^{53}Cr have spin $I = \frac{3}{2}$ and, as a consequence, a nonzero electrical quadrupole moment. The NMR spectrum of ^{53}Cr nuclei is represented by a triplet consisting of a central and two satellite lines. In trigonal symmetry, the resonance frequencies depend on the angle θ between the magnetization and the local symmetry axis. The frequencies of the central and satellite lines are given, in first order, respectively, by the expressions

$$\nu = \nu_0 + \nu_A(3\cos^2\theta - 1), \tag{1}$$

$$\nu = \nu_0 + (\nu_A \pm \nu_q)(3\cos^2\theta - 1). \tag{2}$$

Here ν_0 is the isotropic component of the NMR frequency, ν_A is the anisotropic part of the resonance frequency and ν_q is the value of the quadrupole splitting of the NMR spectrum. For the ^{53}Cr nuclei in cadmium selenochromite values of $\nu_0 = 44.05$ MHz, $\nu_A = -0.55$ MHz and $\nu_q = 0.92$ MHz have been obtained for an oriented single crystal in a magnetic field. The comparison of NMR spectra of doped and undoped polycrystalline samples shows that these values do not depend on the silver concentration at $T = 4.2$ K.

The NMR spectra have been measured by recording the dependence of an echo signal amplitude V_2, on the frequency of RF exciting pulses. The NMR spectrum of ^{53}Cr nuclei in $Cd_{1-x}Ag_xCr_2Se_4$ with $x = 0.015$ is shown in Fig. 1 as an example. For all other investigated samples the NMR spectra are similar to this one.

The cadmium selenochromite is a ferromagnet with very weak cubic anisotropy, therefore this ferromagnet has magnetic domains with magnetization oriented along different lattice directions (magnetic heterogeneity) [7]. Vertical bars in Fig. 1 schematically represent positions of spectral lines, which correspond to quadrupole splittings for

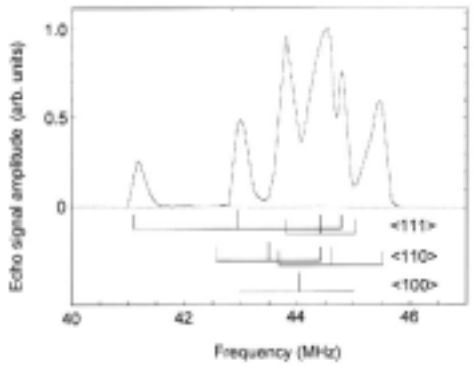

Fig. 1. NMR spectrum of ^{53}Cr nuclei in $Cd_{0.985}Ag_{0.015}Cr_2Se_4$ at $T = 4.2$ K.

different orientations of the magnetization. The number of nonequivalent sites is reduced to two when the magnetization is oriented along ⟨1 1 1⟩ and ⟨1 1 0⟩ directions. The angle θ is equal to a magic angle θ_{mag} (i.e. $\cos^2\theta_{mag} = \frac{1}{3}$) for ⟨1 0 0⟩ direction, therefore one single line is observed for nuclei in these domains. In addition, there is a contribution from nuclei for which the angle θ takes all possible values in the range from 0 up to π which apparently corresponds to nuclei in domain walls. The conformity between the resonance frequency and the angle θ is determined by Eqs. (1) and (2).

The line shape of the NMR spectra was found to depend on the time interval τ between the exciting pulses. This fact reflects a frequency dependence of the transverse relaxation time. The experimental echo signal amplitude V decreases exponentially as the pulse interval τ increases. V is given by the relation

$$V(\tau) = V(0)\exp(-2\tau/T_2), \tag{3}$$

where T_2 is the transverse relaxation time. The T_2 values are found to depend on frequency and are given by circles in Fig. 2. Besides, an increase in the silver concentration results in an increase in the transverse relaxation rate, at various fixed frequencies (Fig. 3).

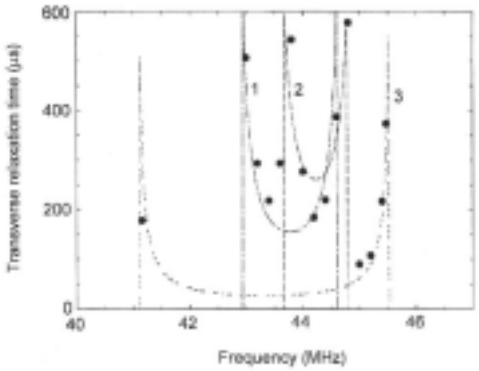

Fig. 2. Frequency dependence of the transverse relaxation time of ^{53}Cr nuclei in $Cd_{0.985}Ag_{0.015}Cr_2Se_4$ at $T = 4.2$ K. The dotted lines represent calculated dependences which are obtained for (1) central transition, (2) quadrupole satellite with $\nu = \nu_A + \nu_Q$ and (3) quadrupole satellite with $\nu = \nu_A - \nu_Q$.

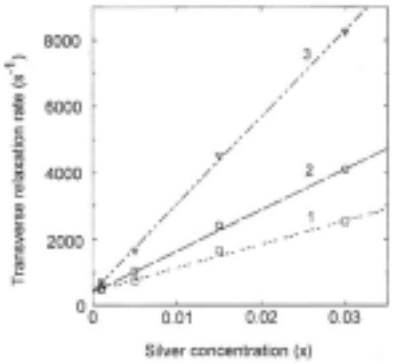

Fig. 3. Dependence of the transverse relaxation rate versus silver concentration at (1) $\nu = 44.8$ MHz, (2) $\nu = 44.6$ MHz and (3) $\nu = 45.4$ MHz.

In the special case of the magic angle θ_{mag} the quadrupole splittings vanish, resulting in a single line of frequency ν_0. For the angles θ in the vicinity of the magic angle the largest transverse relaxation rate is observed.

Traditionally it is supposed that the transverse nuclear relaxation is caused by nuclear–nuclear interactions [8]. The decay of the two-pulse echo signal in the nuclear spin system with magnetic dipole–dipole interactions and interactions of nuclear spins due to virtual magnons in the electron spin system with exchange interactions (Suhl–Nakamura interactions) is theoretically considered in Ref. [9]. An expansion of the echo amplitude as a power series in τ does not contain any terms which are of odd degree in τ. On the other hand, an expansion of the exponent in Eq. (3) as a power series in τ has terms of odd degree in τ which are essentially not equal to zero. Thus, it is obvious that the model of nuclear–nuclear interactions without microscopic inhomogeneity cannot be adopted for the analysis of experimental results.

We assume that the orientation of the magnetization vector in a sample can take any of the possible values. In this case an echo signal at each of the spectrum frequencies in Fig. 1 is caused by nuclear spins with the angle θ determined by Eqs. (1) and (2). The dependence of the relaxation rate on frequency reflects the dependence of T_2 on θ.

In Ref. [5], the attenuation of the two-pulse spin-echo signal from zero–quadrupole nuclei of ^{57}Fe in monocrystal films of iron–yttrium garnet is studied. It is shown that the longest time of attenuation of the echo signals is observed near the magic angle θ. The model of spectral diffusion is used for the analysis of experimental results in Ref. [5]. The directional fluctuations of the magnetization are considered as the source of fluctuations of local magnetic fields on nuclei in lattice sites with uniaxial symmetry. The advanced approach in Ref. [5] is used for the analysis of the frequency dependence of ^{53}Cr nuclei transverse relaxation time in Ag-doped $CdCr_2Se_4$.

The recording of NMR spectra by measuring the frequency dependence of the echo signal amplitude is accompanied by the selective excitation of a spectral line. Not all of the sample nuclear spins are excited, the excitation is observed only for the spins with resonance frequencies near the excitation frequency. This case of the transverse relaxation processes for quadrupole nuclei has theoretically been analyzed within the framework of the spectral diffusion model in Ref. [6].

Analyzing the experimental results, we assume that the transverse relaxation time T_2 has isotropic T_{2i} and anisotropic T_{2A} parts

$$T_2^{-1} = T_{2i}^{-1} + T_{2A}^{-1}. \tag{4}$$

The frequency dependence of T_2 is due to the anisotropic part only. We consider the dynamic inhomogeneity of magnetization orientation as the source of the local field fluctuations on nuclei. This approach follows the one presented in Ref. [5]. For a change $d\theta$ in the angle between the magnetization and the local symmetry, the resonance frequency changes by

$$d\nu = -3\pi \sin(2\theta)\, d\theta, \tag{5}$$

where $\pi = \nu_A$ for the central transition and $\pi = (\nu_A \pm \nu_q)$ for the quadrupole satellites. Eq. (5) is obtained by direct differentiation of Eqs. (1) and (2) with respect to θ.

If the magnetization forms an angle θ with the local symmetry axis and this angle fluctuates in the range $\theta \pm d\theta$, it results in fluctuations of resonance frequencies. The line width of NMR frequency fluctuations according to Eq. (5) is,

$$\sigma = |3\pi \sin(2\theta)\, d\theta|. \tag{6}$$

Using the expressions for the attenuation of a two-pulse echo signal obtained in Ref. [6], we find that the exponential decay of echo signals with a parameter depending on the line width σ takes place for the fast Lorentzian process

$$T_{2A}^{-1} = 2\sigma = K_L \pi \sin(2\theta) \tag{7}$$

and for the fast Gaussian process

$$T_{2A}^{-1} = 2\sigma^2 \tau_c = K_G \pi^2 \sin^2(2\theta), \tag{8}$$

where τ_c is the correlation time for random process, factor $K_L = 6\, d\theta$ and factor $K_G = 18\, d\theta^2 \tau_c$.

In comparing the calculated dependences with the experimental ones the following procedure was used. Frequencies in the range 41–47 MHz were selected in successive steps. According to the above mentioned values of parameters ν_0, ν_A and ν_q, the value of the angle θ was determined using Eqs. (1) and (2). The transverse relaxation time for the corresponding frequency was calculated using the value of the angle θ obtained and Eqs. (7) and (8). The calculations were carried out using an IBM PC. The T_{2i}, K_L and K_G values resulting from various runs of the program were selected so as to provide the best agreement of calculated dependences with experimental data.

On the basis of this computation it is concluded that the Gaussian process describes the experiment better than the Lorentzian one. The dotted lines in Fig. 2 show calculated dependences obtained for $T_{2i} = 606\ \mu s$ and $K_G = 16.0 \times 10^{-3}\ \mu s^{-1}$. Line 1 corresponds to the central transition $\pm\frac{1}{2} \leftrightarrow \mp\frac{1}{2}$. The lines 2 and 3 correspond to the quadrupole satellites with $\pi = \nu_A \pm \nu_q$ (transitions $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$). The best approximation of the experimental results is obtained with identical values of the isotropic part T_{2i} both for the central and satellite lines.

It is of interest to consider the most probable mechanisms of the directional fluctuations of magnetization. Doping of the cadmium selenochromite with silver produces, as a result of charge compensation, the Cr^{4+} impurities with t_{2g}^2 configuration. The spin–orbit coupling of these ions should increase the magnetic anisotropy. We assume that the

electron exchange between the Cr^{4+} ions and the valence band turns these ions into dynamic defects with some finite lifetime.

Due to magnetic heterogeneity and the existence of domain walls in a sample, a set of all possible θ values is observed. The occurrence of the Cr^{4+} ion in some lattice positions results in a reorientation of the local magnetization and therefore a change in angle θ. Thus, the dynamic effects of defects with strong spin–orbit coupling are considered to be the source of fluctuations of magnetization orientation.

The increase in the impurity concentration should result in an increase in the rate of magnetization reorientation, i.e. a reduction of the correlation time. On the other hand, this increase should enhance the amplitude of fluctuations. Assuming that, for small impurity concentrations, both the reduction in the correlation time and the increase in the fluctuation amplitude are simply proportional to the Ag^{+} ion concentration, we obtain a linear variation of the transverse relaxation rate with silver concentration (Fig. 3).

3. Conclusions

The transverse magnetic relaxation rate of ^{53}Cr nuclei in silver-doped ferromagnetic $CdCr_2Se_4$ has been investigated. It is shown that the dependence of nuclear spin-echo decay on resonance frequency is described by the Gaussian process of spectral diffusion. Directional fluctuations of the magnetization are proposed as the origin of NMR frequency fluctuations for the octahedral sites with trigonal distortion. It is shown that such fluctuations arise from dynamic defects with a strong spin–orbit coupling represented by Cr^{4+} ions.

Acknowledgements

This work was supported in part by the International Soros Science Education Program through grant No. SPU062005.

References

[1] J.R. Klauder, P.W. Anderson, Phys. Rev. 125 (1962) 912.
[2] H.E. Rorschach, J. Magn. Res. 67 (1986) 519.
[3] A.M. Portis, A.C. Gossard, J. Appl. Suppl. 31 (1960) 205S.
[4] S.K. Ghosh, Phys. Rev. B. 5 (1972) 174.
[5] G.N. Abelyashev, S.N. Polulyakh, V.N. Berzhanskij, N.A. Sergeev, J. Magn. Magn. Matter. 147 (1996) 305.
[6] S. N Polulyakh, N.A. Sergeev, JETF 108 (1995) 14.
[7] G.N. Abelyashev, V.N. Berzhansky, Yu.V. Fedotov, N.A. Sergeev, Pisma v JETF. 45 (1987) 34.
[8] M.I. Kurkin, E.A. Turov, NMR in Magnetically Ordered Materials and its Applications, Nauka, Moskow, 1990, p. 248.
[9] D. Weltz, Physica B 141 (1986) 121.