Magnetic heterogeneity of $CdCr_2Se_4$-based ferromagnetic semiconductors

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A method is proposed for separating the nuclear-spin-echo signals of nuclei in domains and of nuclei in walls. It is shown by this method that ferromagnetic semiconductors of the $CdCr_2Se_4$ type are magnetically heterogeneous.

No experimental data have been available on the structure of the magnetic phases in magnetic semiconductors based on chromium chalcogenide spinels in a multidomain state. Since the response of an unsaturated magnetic material to an external agent is determined to a significant extent by the nature of the domain structure, there is a need for a study of this structure in bulk crystals of ferromagnetic semiconductors. In the present letter we report an NMR study of the composition of the magnetic phases in $CdCr_2Se_4$-based crystals. We have determined the directions of the magnetization vector M in domains in a zero external magnetic field. The NMR at the ^{53}Cr nuclei ($I = 3/2$) is detected by a spin-echo method at $T = 4.2$ K.

The Cr atoms in the $CdCr_2Se_4$ spinel structure occupy trigonally distorted octahedral positions. The NMR frequency is thus determined by not only the isotropic

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hyperfine interaction but also the magnetic anisotropic and electric quadrupole hyperfine interactions. The NMR spectrum of ^{53}Cr depends on the angle between the magnetization M and the [111] directions, which are principal axes of the magnetic anisotropic and quadrupole hyperfine interactions. If the values of the constants of all the hyperfine interactions for the nucleus under study are known, the angles between M and the [111] axes can be determined by analyzing the NMR spectra of nuclei in domains. The hyperfine constants for ^{53}Cr nuclei in $CdCr_2Se_4$ were determined in Ref. 1 through an analysis of the angular dependence of the NMR spectrum of a single crystal in a saturating external field H. In multidomain $CdCr_2Se_4$, however, the NMR spectrum of the ^{53}Cr nuclei in domains overlaps an intense and broad spectrum of nuclei in domain walls; so far, it has not been found possible to separate these spectra by conventional methods. These spectra were accordingly interpreted in Ref. 2 as the result of a random distribution of the directions of M in the crystal. The simultaneous excitation of nuclei in domains and in walls in $CdCr_2Se_4$ results in not only a smearing of the NMR spectrum but also a complex shape for the spin-echo signal. This shape can be described as the result of a superposition of two components having different relaxation times T_2^* (Fig. 1). The component with the longer time T_2^* stems from the echo signal from nuclei in domains. In a measurement of the NMR spectra by the spin-echo method, the signal arrives at the input of the storage device at a time determined by a strobing pulse, which turns on a switching device. In the standard recording method, the strobe pulse is applied at the time 2τ, at which the echo signal is at a maximum (τ is the time interval between the exciting pulses). The components of the spectrum are not separated in this case, and the shape of the spectrum (Fig. 2a) is similar to that shown in Ref. 2. In the present study we have succeeded in separating the components, by applying the strobe pulse at the time $2\tau + \Delta t$, where Δt is chosen to satisfy the conditions $T_2^{*w} < \Delta t < T_2^{*d}$ (Fig. 1). In the course of this procedure we distinguish a component of the spectrum which is due to a resonance of nuclei in domains having the longer value of T_2^*. Figure 2b shows the spectrum of ^{53}Cr nuclei in

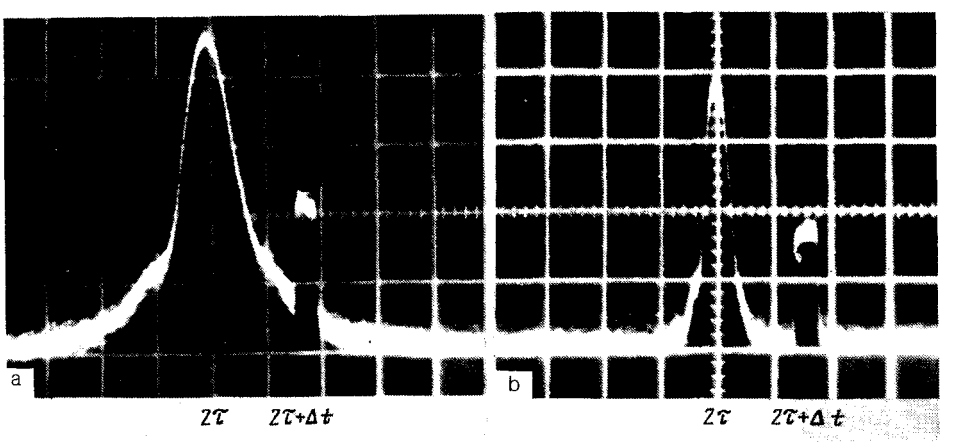

FIG. 1. Oscilloscope traces of spin-echo signals of ^{53}Cr nuclei in $CdCr_2Se_4$. a—During excitation in domains and domain walls; b—in domain walls.

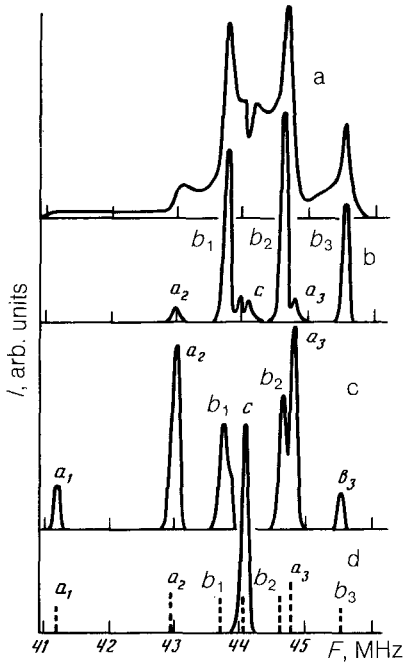

FIG. 2. NMR spectra of ^{53}Cr nuclei. a, b—In $CdCr_2Se_4$; c—in $Cd_{0.985}Ag_{0.015}Cr_2Se_4$; d—in $Cd_{0.9}In_{0.1}Cr_2Se_4$. Lines a_2, b_2, and c correspond to the transition $+1/2 \leftrightarrow -1/2$.

domains in multidomain $CdCr_2Se_4$ found under these conditions. It can be seen from a comparison of Figs. 2a and 2b that the method proposed for recording the NMR spectra substantially improves the resolution of the spin-echo method, and it has permitted the first recording of the spectrum of nuclei in domains in $CdCr_2Se_4$. The data found from an analysis of this spectrum have been used to identify the magnetic phases in $CdCr_2Se_4$-based ferromagnetic semiconductors in a multidomain state. According to Ref. 3, the vector M in the domains of a cubic ferromagnet at $H = 0$ may—depending on the relation between the first and second anisotrophy constants (K_1 and K_2, respectively)—be oriented along one of the principal crystallographic directions [111], [110], or [100] (the phases Φ_{111}, Φ_{110}, and Φ_{100}, respectively). According to ferromagnetic-resonance data,[4] the relation $K_1 > 0$ holds in pure $CdCr_2Se_4$, and the phase Φ_{110} should not be seen in the NMR spectrum. However, the spectrum (Fig. 2b) has a fine structure which reflects the presence of three phases simultaneously. (Lines a_2 and a_3 belong to the Φ_{111} phase; b_1, b_2, and b_3 to the Φ_{110} phase; and c to the Φ_{100} phase.) The dashed lines in Fig. 2 are the frequencies of the most intense lines in the NMR spectrum of ^{53}Cr nuclei in $CdCr_2Se_4$, according to calculations for various orientations of M with the help of the hyperfine-interaction constants from Ref. 1. In a comparison with the frequencies of the NMR spectrum which we found for nuclei in domains in multidomain $CdCr_2Se_4$, it turned out that each line in the NMR spectrum of the nuclei in domains corresponds very accurately to a calculated frequency found for an orientation of M along one of the three directions [111], [110], and [100]. This result means that domains with a magnetization parallel to the principal cyrstallographic directions coexist in multidomain $CdCr_2Se_4$. The Φ_{110} phase is the most intense.

The volumes (ρ) of the magnetic phases, found from the intensities of the lines of the transition $+1/2 \leftrightarrow -1/2$, are $\rho_{110} = 84\%$, $\rho_{111} = 8\%$, and $\rho_{100} = 8\%$. Since the phase diagram of a cubic ferromagnet constructed on the basis of K_1 and K_2 alone does not contain regions in which all three phases can coexist,[3] it can be suggested that the existence of phases in $CdCr_2Se_4$ is a result of the action of factors which have not been considered in this diagram. Among such factors are magnetoelastic effects and a nonuniformity of the distribution of impurity chromium ions of different valences over the sample. For $CdCr_2Se_4$, where K_1 and K_2 have record-low values, the effects of these factors may be substantial.

As the anisotropy constants increase (the magnitudes and signs of these constants can be controlled by an appropriate doping), the role of the magnetocrystalline anisotropy in the formation of the phase composition of $CdCr_2Se_4$ should increase. Accordingly, we used the method described above to study the NMR spectra of ^{53}Cr nuclei in some doped crystals: $CdCr_2Se_4$: Ag and $CdCr_2Se_4$ (Fig. 2, c and d). With increasing Ag concentration, the value of K_1 goes negative, increasing in magnitude.[4] Doping with In increases K_1, which remains positive.[5] The NMR spectrum of $CdCr_2Fe_4$ (Fig. 1d) is left with a single line corresponding to the Φ_{100} phase (line c). Since the stability region of the Φ_{100} phase is determined by the condition $K_1 \geqslant 0$, this result agrees with the behavior of K_1 during doping. During doping of $CdCr_2Se_4$ with silver, there is a redistribution of magnetic phase (Fig. 1d). The phase Φ_{100} disappears, and the phase Φ_{111} (line a_1, a_2, and a_3) becomes predominant ($\rho_{111} = 75\%$; $\rho_{110} = 25\%$).

In summary, we have succeeded in separating the NMR signals from nuclei in domains and in walls. The results show that $CdCr_2Se_4$ crystals in a multidomain state are magnetically heterogeneous, and the equilibrium direction of M in the domains is not the same as the direction calculated from data on the anisotropy constants measured by the ferromagnetic-resonance method.

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