Magnetic resonance in disordered magnets of the $Cd_{1-x}Zn_xCr_2Se_4$ system

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Magnetic resonance in disordered magnets of the $Cd_{1-x}Zn_xCr_2Se_4$ system is investigated. The single crystals of this system are spiral antiferromagnets for $x \geqslant 0.43$, ferromagnets for $x \leqslant 0.38$, and spin glasses for $x \approx 0.4$. The localized magnetic moments of Cr^{3+} ions in the single crystals of this system are located at the sites of the simple cubic lattice so that the spin glasses of this system correspond to the random interaction model rather than the random site model. The cubic magnetocrystalline anisotropy energy of the single crystals of this system may be varied continuously over a broad range from 10^3 to 10^5 erg·cm^{-3} by doping such crystals with 0 to 5% mol.% Ag. The anomalous shift of the magnetic resonance line in spin glasses is found to be the result of the noncollinearity of their magnetic structure. The magnitude of this shift is determined by the modification of the exchange interactions due to isotropic volume magnetostriction and is not related to the magnitude of the magnetocrystalline anisotropy energy or the Dzyaloshinskii-Moriya interaction level, nor to the dynamic shift due to dipole broadening of the magnetic resonance line.

INTRODUCTION

A number of authors have analyzed magnetic resonance in spin glasses (SG). It has been established for many different classes of spin glasses that anomalous reduction in the magnitude of the magnetic resonance field H_R is observed with decreasing temperature in spin glasses at a fixed microwave radiation frequency ω.[1-9] Classical electron paramagnetic resonance (EPR) is observed in SG at temperatures T somewhat greater than the temperature T_g of transition to the spin glass state. Here we have written $H_R = \omega/\gamma$, where γ is the gyromagnetic ratio, which ordinarily corresponds to a g factor of near two. Such behavior is observed over a temperature range $T \gg T_g$. There is a significant shift of the resonance field denoted by H_i (H_i is the internal effective field) at sufficiently low temperatures $T < 3T_g$. Magnetic resonance is therefore observed in SG for

$$H_R = \omega/\gamma - H_i. \tag{1}$$

The quantity H_i is a monotonically decreasing function of temperature, and equals ~ 1 kOe at temperatures of ~ 10 K. Interestingly, the order of magnitude of H_i does not depend on the different SG parameters, i.e., it is identical in all SG of different classes. H_i is likewise always positive and independent of crystal orientation relative to the external magnetic field. In other words, it is as though the external magnetic field direction in SG is always the easy axis of magnetization. Such a view of relation (1) derives from the observation of a shift of H_R corresponding in magnitude to the anisotropic field H_a in classical paramagnets at a sufficiently high magnetocrystalline anisotropy energy E_a. In this case, however, both the sign and magnitude of the shift depend on crystal orientation with respect to the external field H. Ordinarily, H_a is substantially below 1 kOe. It is well known that, such an anomalous shift of the resonance field has been observed in both amorphous[1] and crystalline[2,3] spin glasses.

No satisfactory explanation of the nature of this phenomenon has been offered to date. One could suppose that an external magnetic field induces a unidirectional anisotropy in the SG's. This would be possible with sufficiently large values of the Dzyaloshinskii-Moriya interaction parameter such as in spin glasses based on transition metal alloys. Such an explanation has been offered in many studies, e.g., Refs. 1 and 4. Indeed, unidirectional anisotropy has been observed in SG with large values of this parameter below the transition temperature T_g together with shifted hysteresis loops following cooling of the SG in an external magnetic field. These effects, however, are absent at temperatures above the transition temperature T_g and the Dzyaloshinskii-Moriya interaction is not strong in all spin glasses.

The resonance field shift in spin glasses is accompanied by significant broadening of the absorption line.[1-9] The absorption linewidth Γ of microwave radiation grows exponentially as the temperature decreases

$$\Gamma - \Gamma_0 = \Gamma_1 \exp(-T/T_0), \tag{2}$$

where Γ_0 is the absorption linewidth at high temperatures corresponding to ordinary EPR; Γ_1 and T_0 are empirical parameters, with $\Gamma_1 \gg \Gamma_0$ and $T_0 \sim T_g$. The dynamical shift H_R associated with dipole broadening of the absorption line is in most cases substantially below H_1 in SG's and is ~ 100 Oe for $\omega/2\pi \sim 10$ GHz and $T \sim T_g$ (Ref. 3). According to calculations[5] the dynamical shift of the resonance field would have a power-law dependence on the parameter $\varepsilon = (T - T_g)/T_g$ as $T \to T_g$, while the ratio of the linewidth to the magnitude of this shift would drop off sharply in proportion to $1/\omega\tau$, where $\tau \sim \varepsilon^{-z\nu}$ is the characteristic relaxation time of the spin subsystem; z and ν are critical indices; H_i would also vary as $\propto \omega^{-1}$ for $\omega\tau \gg 1$, which was not observed in Refs. 6–8 when the frequency ω was tuned over the range 2–35 GHz. Indeed, as demonstrated by Ref. 5, the linewidth Re Γ associated with dipole broadening, and the dynamical shift Im Γ, have the following dependence on τ and ω:

$$\mathrm{Re}\,\Gamma \propto \frac{\tau}{4+\tau^2\omega^2} \sum_i \frac{1}{r_i^6}, \tag{3}$$

$$\mathrm{Im}\,\Gamma \propto \frac{\omega\tau^2}{4+\tau^2\omega^2} \sum_i \frac{1}{r_i^6}, \tag{4}$$

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where the sum over i is a lattice sum for the dipole-dipole interactions between chaotically distributed spins; r_i are the distances between the spins. Note that the analogous sum for the spins ordered among the sites of the simple cubic lattice is exactly equal to zero when the spins are oriented in parallel, and is relatively small when they are randomly oriented. It would therefore be interesting to investigate magnetic resonance in SG's in which the spins are ordered at the sites of the simple cubic lattice. Single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system for $x \sim 0.4$ are such spin glasses.

In this paper we investigate magnetic resonance in single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system in which the Dzyaloshinskii-Moriya interaction is not significant, and their magnetocrystalline anisotropy energy can be controlled over a broad range of 10^3–10^5 erg·cm^{-3} by silver doping at levels up to 5 mol.%. Analyzing single-crystal SG permits an independent measurement of the contributions to the resonance field shift from H_i and from magnetocrystalline anisotropy. This cannot be achieved by analyzing polycrystalline or amorphous spin glasses.

1. SAMPLES AND EXPERIMENTAL METHOD

Single crystals synthesized by spontaneous crystallization from a melt solution at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR were analyzed. Single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system are normal spinels with a cubic crystalline structure. Their magnetic properties are due to the localized magnetic moments of the Cr^{3+} ions at the octahedral sites of the spinel structure. Magnetic ordering is established by direct exchange interaction between Cr^{3+} and indirect superexchange between these ions involving Se^{2-} as well as Cd^{2+} or Zn^{2+} ions. Both nearest neighbor interaction and interaction between the next nearest neighbors are significant in this case.[10] The single crystals of this system are spiral antiferromagnets (AFM) for $x \geqslant 0.43$; ferromagnets (FM) for $x \leqslant 0.38$, and spin glasses for $x \approx 0.4$.[11-13]

The cubic magnetocrystalline anisotropy energy of undoped single crystals of this system is relatively small, $E_a \sim 10^3$ erg·cm^{-3}. The E_a of single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system was found to vary from 10^3 to 10^5 erg·cm^{-3} from Ag doping up to levels of 5 mol.% on a rotating sample magnetometer whose design is described in Ref. 14. Silver doping will not only increase the magnetocrystalline anisotropy energy but will also increase the range of x where such crystals become spin glasses.[11,15] For example, the single crystals of this system with $x = 0.4$ are SG with $T_g = 20$ K and $E_a \sim 10^3$ erg·cm^{-3}, while for $x = 0.46$ they are antiferromagnets. Doped single crystals with $x = 0.46$ are spin glasses with $T_g = 17$ K and $E_a \sim 10^4$ erg·cm^{-3} at a silver dopant concentration of ~ 2 mol.% and with $T_g = 37$ K and $E_a \sim 10^5$ erg·cm^{-3} at 5 mol.% Ag.

These single crystals were shaped as proper octahedrons with sides of ~ 2 mm. Wafers parallel to one of the crystallographic planes (100), (110), or (111) were cleaved from the octahedrons. Square, rectangular, or isosceles triangle wafers were obtained. Disks were then cleaved from these wafers.

The measured values of H_R and even Γ were found to be essentially independent of wafer shape. Polishing the wafers likewise had no significant effect on the magnetic resonance linewidth of disordered magnets of this system. Wafer thickness was found to have a much stronger effect; this thickness was varied over a range of 80–400 μm. The demagnetizing factors of the wafers were found to vary with wafer thickness. This caused a significant shift of H_R. Direct magnetization measurements of the samples on a vibrating sample magnetometer were employed to test the correlation between H_R and variations in the demagnetizing factors of these wafers. The magnetic resonance linewidth grew with increasing wafer thickness, due to magnetization inhomogeneities in the thick wafers. Only rather thin ($\sim 100\,\mu$m) wafers represent a satisfactory model of an ellipsoid that is uniformly magnetized in an external magnetic field.

The conductivity of these samples depended on their degree of doping and varied over a range 10^{-1}–10^{-6} Ω^{-1}·cm^{-1} at room temperature for silver concentrations from 0 to 5 mol.%. Figure 1 shows the temperature dependence of the resistivity of doped single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system. The samples were cut into $2 \times 2 \times 0.5$ mm^3 wafers with contact pads deposited on the polished surface of these wafers. A chrome layer $\sim 0.1\,\mu$m thick was initially deposited. A copper layer of $\sim 0.2\,\mu$m was then deposited on top of this layer. Copper microwires 30 μm in diameter were then attached to these wafers. Sample resistivity was measured by the four-probe technique. The conductivity of the samples drops as the temperature decreases. The skin-effect can be neglected in this case. Indeed, results of magnetic resonance studies on undoped spin glasses with $x = 0.4$ were found to be analogous to results for spin glasses with $x = 0.46$ and a doping level of ~ 2 and 5 mol.% Ag.

The magnetic resonance studies were carried out on an automated Radiopan x-ray EPR spectrometer employing an RCX-102 rectangular cavity with a q of $5 \cdot 10^3$. The TE_{102} mode is the fundamental cavity mode. All measurements were carried out at a microwave frequency near 9.1 GHz.

We designed a low-temperature spectrometer adapter for experiments in the temperature range 4.2–300 K. This unit consisted of a quartz Dewar vessel with a 10 mm outer

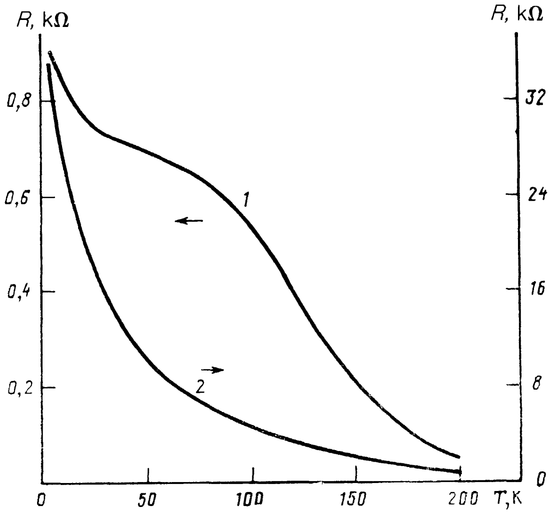

FIG. 1. Temperature dependence of the resistance R of $2 \times 2 \times 0.5$ mm^3 wafers of doped single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system for $x = 1$ and 4 mol.% Ag (curve 1), $x = 0.5$ and 0.5 mol.% Ag (curve 2).

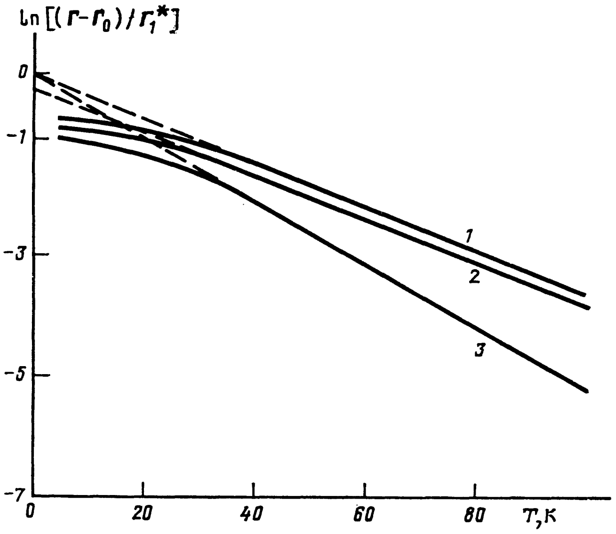

FIG. 2. Temperature dependence of the width of the magnetic resonance line Γ of disordered magnets of the $Cd_{1-x}Zn_xCr_2Se_4$ system ($\Gamma_1^* = 10$ kOe): 1—$x = 0.43$ and 2 mol.% Ag; 2—$x = 0.46$ and 5 mol.% Ag; 3—$x = 0.43$.

diameter. The Dewar vessel was inserted into the cavity whose walls were maintained at room temperature during the experiment. Gaseous helium was pumped through the Dewar vessel. The gas temperature was controlled by a temperature stabilization system, which stabilized the temperature of the sample to better than 0.5 K. The sample could be rotated about the vertical axis without removing it from the cavity. The sample temperature was measured by means of a $Cu–CuFe_{0.1}$ thermocouple.

2. EXPERIMENTAL RESULTS

2.1. Studies of the magnetic resonance linewidth

Ordinary electron paramagnetic resonance with a temperature-independent $H_R = \omega/\gamma$ is observed in all samples of the $Cd_{1-x}Zn_xCr_2Se_4$ system for different x and with different silver dopant levels at temperatures above 150 K. The gyromagnetic ratio γ was found to correspond to a g factor of 1.98. The width $\Gamma_0 \sim 100$ Oe corresponding to the peak-to-peak distance of the derivative of the EPR line is associated with ordinary dipole broadening, and decreases as the temperature drops from 300 to 150 K due to exchange narrowing.[16] A further decrease in temperature leads to an exponential growth in the resonance linewidth of disordered magnets with $x \sim 0.4$. Anomalous broadening of Γ to several kOe is observed in spin glasses at 4.2 K. Such broadening becomes noticeable as early as temperatures $\sim 3T_g$.

The relation $\Gamma(T)$ is accurately described by Eq. (2) for $T \gg T_g$ with a parameter $\Gamma_0 \sim 100$ Oe, $\Gamma_1 \sim 10$ kOe, and $T_0 \sim T_g$, as shown in Fig. 2. The temperature dependences of $\ln[(\Gamma - \Gamma_0)/\Gamma_1]$ reveal a knee at a certain $T \sim T_g$. An extrapolation of these relations from the high-temperature range as $T \rightarrow 0$ intersects the x axis at virtually the same point for weakly and strongly anisotropic disordered magnets. The values of parameters Γ_1 are therefore not determined by the magnitude of the magnetocrystalline anisotropy energy.

The table provides the parameter values for two SG and a single disordered AFM with a concentration $x = 0.43$ close to the concentration range of spin glasses. We measured the Néel temperature T_N of the antiferromagnets by means of a rotating sample magnetometer as outlined in Ref. 17 and thereby identified long-range AFM-ordering. Analogous results were obtained from spontaneous magnetostriction measurements in AFM's of the $Cd_{1-x}Zn_xCr_2Se_4$ system. This measurement method is described in Refs. 18, 19. The values of T_g were determined for the SG's from the temperature dependence of the real χ' and imaginary χ'' parts of the magnetic susceptibility in an 83 Hz alternating magnetic field.

The magnetocrystalline anisotropy energies were measured by means of a rotating sample magnetometer. Results from rotating sample magnetometer measurements of the magnetocrystalline anisotropy energy were found to be in good agreement with results from measurements of E_a based on the angular dependence of the resonance field H_R obtained by rotating the crystal relative to the external magnetic field. In this case the disk sample was rotated about its axis of symmetry so that the external field remained perpetually in the plane of the disk. Figure 3 shows such a relation for spin glass with $x = 0.52$ and 5 mol.% Ag at 16 K. Clearly, the magnitude of the anisotropy field ~ 100 Oe and the easy magnetization axis coincides with the [111] axis of the crystal.

Studies of the temperature dependence of the magnetic resonance linewidth of disordered AFM's of the $Cd_{1-x}Zn_xCr_2Se_4$ system have demonstrated that relation (2) holds in this case at temperatures above the Néel temperature. Here, the parameter Γ_1 rises as x approaches the concentration range of spin glasses. The parameter Γ_1 that characterizes anomalous broadening of the magnetic resonance line in disordered magnets is therefore dependent on their degree of disorder and is independent of the magnetocrystalline anisotropy energy. This confirms the hypothesis[1] that such broadening is due to the chaotic distribution of local exchange fields in disordered magnets. These fields become significant in magnitude at levels substantially above the transition temperature T_g or T_N due to the onset of long-range magnetic order in the system.

2.2. Temperature dependence of the resonance field

The temperature dependence of the resonance field H_R for $\omega/2\pi = 9.1$ GHz for spin glasses with $x = 0.43$ and 2

TABLE I. Characteristic parameters of disordered magnets of the $Cd_{1-x}Zn_xCr_2Se_4$ system.

x	mol. %	T_g, K	T_N, K	T_0, K	E_a, erg·cm^{-3}	Γ_1, kOe
0,43	2	20	—	27	10^4	10
0,46	5	37	—	26	10^5	8
0,43	0	—	13	19	10^3	10

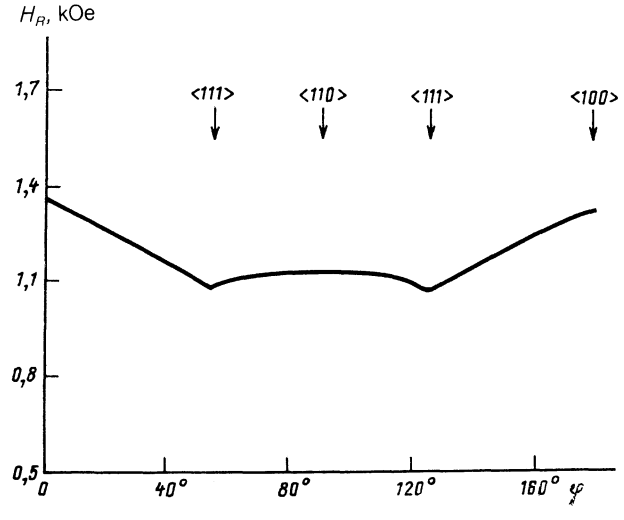

FIG. 3. The resonance field magnitude as a function of the angle between the direction of this field and the [011] axis of a crystal with $x = 0.53$ doped by 5 mol.% Ag at 16 K. The external field is parallel to the (110) crystal plane.

mol.% Ag is shown in Fig. 4. This sample is a $3\times3\times0.4$ mm^2 wafer with a plane parallel to the (100) plane of the crystal. Resonance was observed in two cases: with an external field $H_\parallel$ parallel to the plane of the wafer and with an external field $H_\perp$ perpendicular to this plane. The field direction in both cases coincides with the [100] direction of the crystal. The relations $H_R(T)$ were found to be in good agreement with Kittel's equations in both cases at temperatures above 80 K:

$$(\omega/\gamma)^2 = H_\parallel [H_\parallel + 4\pi(n_\perp - n_\parallel)M], \qquad (5)$$

$$\omega/\gamma = H_\perp - 4\pi(n_\perp - n_\parallel)M, \qquad (6)$$

where $n_\parallel$ and $n_\perp$ are the demagnetization factors of the sample parallel and perpendicular to the plane of the wafer; M is the magnetization of the sample. Families of $M(H)$ curves for different temperatures and wafer orientations relative to the external magnetic field were measured to test these relations. The values of $M(H, T)$, $n_\parallel = 0.1$ and $n_\perp = 0.8$ measured on the vibrating sample magnetometer, were substituted into Eqs. (5) and (6). For $4\pi M \ll H_R$ relations (5) and (6) can be approximated by

$$H_\parallel \approx \omega/\gamma - 2\pi M(n_\perp - n_\parallel) + \ldots, \qquad (7)$$

$$H_\perp = \omega/\gamma + 4\pi M(n_\perp - n_\parallel). \qquad (8)$$

It is clear from Fig. 4 that these relations hold in the temperature range 80–140 K. The experimental values are observed to deviate from relations (5) and (6) at lower temperatures. This is even evident in the fact that, rather than experiencing a monotonic rise, the resonance field $H_\perp$ begins to drop off sharply as $T \to 0$ and even falls below ω/γ at temperatures of less than 10 K. It was found that the experimental relations $H_R(T)$ could be described in a manner analogous to Eq. (1) as follows:

$$(\omega/\gamma)^2 = (H_\parallel + H_i)[H_\parallel + H_i + 4\pi(n_\perp - n_\parallel)M], \qquad (9)$$

$$\omega/\gamma = H_\perp + H_i - 4\pi(n_\perp - n_\parallel)M, \qquad (10)$$

where H_i is a certain external effective field that is always positive and independent of crystal orientation relative to the direction of the external magnetic field, if we take into account the small, orientation-dependent addition H_α of the magnetocrystalline anisotropy field. Using the experimental relations $H_R(T)$ and $M(H, T)$ we can determine the temperature relations $H_i(T)$ from Eqs. (9) and (10) for the two cases where the external field is perpendicular and parallel to the plane of the wafer. These relations, which are shown in Fig. 4, do not coincide since H_i depends on the magnetization of the sample. The magnetization in the plane of the wafer with a corresponding resonance field $H_\parallel$ is lower than in the direction perpendicular to this plane with resonance field $H_\perp$ at the same frequency. Consequently, H_i grows as a function of the sample magnetization, as we see in Fig. 4. Analogous relations $H_i(T)$ are observed for SG samples

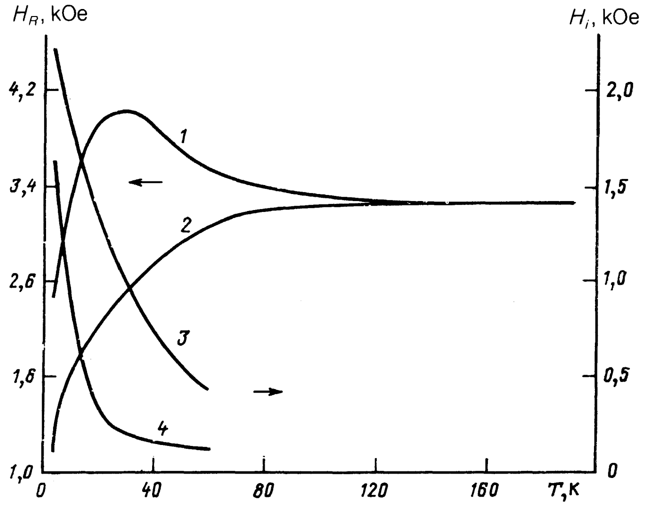

FIG. 4. Temperature dependence of the resonance field H_R (1, 2) and the effective external field H_i (3, 4) for SG with $x = 0.43$ doped by 2 mol.% Ag; 1, 3—field applied along the [100] axis of the crystal perpendicular to the wafer plane; 2, 4—field parallel to the wafer plane and the [010] axis.

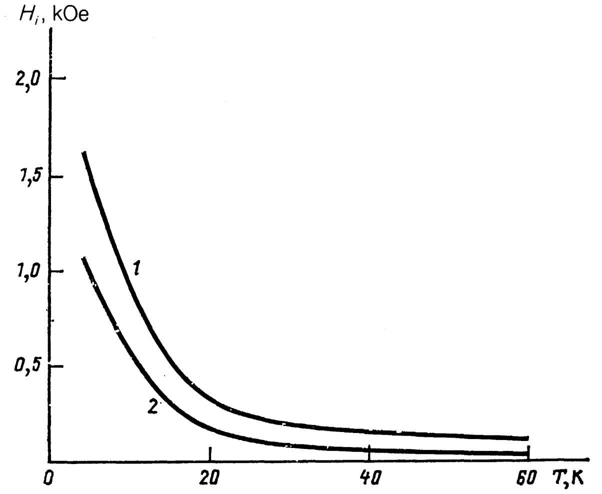

FIG. 5. Temperature dependence of the effective internal field H_i for spin glasses with $x = 0.43$ doped by 2 mol.% Ag at a wafer thickness of 0.4 mm (curve 1) and 0.8 mm (curve 2). The external field is parallel to the wafer plane.

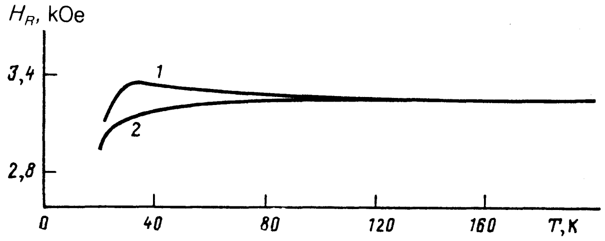

FIG. 6. Temperature dependence of the resonance field for an ordered $ZnCr_2Se_4$ antiferromagnet. The external magnetic field is perpendicular to the plane of the wafer along the [100] axis of the crystal (curve 1) and parallel to the plane in the [010] direction (curve 2).

with different thicknesses, sample shapes, and concentrations x. Figure 5 shows how H_i depends on wafer thickness.

Unfortunately, only a qualitative analysis of these $H_i(T)$ relations is possible. The temperature dependence of H_i is measured with different magnetizations and different external magnetic field levels. An $H_i(T)$ relation measured in a uniform external field would be physically meaningful if it were possible to tune the microwave radiation over a broad frequency range. Such an experiment cannot be carried out on an x ray spectrometer. It is nonetheless possible to claim that an anomalous shift of the magnetic resonance line has been observed in the SG of the $Cd_{1-x}Zn_xCr_2Se_4$ system at temperatures $T \leqslant 3T_g$. This shift is caused by the onset of a certain effective internal field that is always directed parallel to the external magnetic field.

Such a shift of the magnetic resonance line is found to occur not only in SG's and reentrant FM's of the $Cd_{1-x}Zn_xCr_2Se_4$ system, but also in spiral AFM's. It subsequently turned out that this shift is even found in disordered FM's and ordered $ZnCr_2Se_4$. Figure 6 shows the temperature dependence of H_R for a $ZnCr_2Se_4$ single crystal, a spiral AFM with a Néel temperature $T_N = 21$ K. The $H_R(T)$ relations for an ordered spiral AFM at temperatures above the Néel temperature are clearly analogous to these relations for spin glasses. Resonance is observed in AFM only at higher microwave radiation frequencies for $T < T_N$, due to the gap in the excitation spectrum of the antiferromagnet.

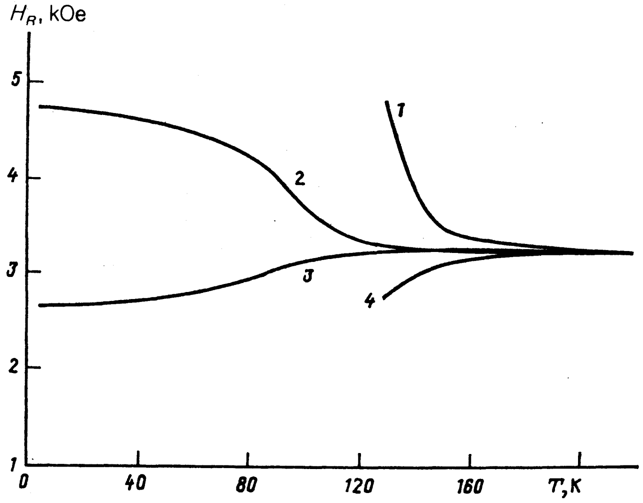

FIG. 8. Temperature dependence of the resonance field magnitude H_R along the [100] crystal axis for ordered FM's: 1—$x = 0$ (magnetic field perpendicular to the wafer plane), 2—$x = 0.2$ (field perpendicular to the plane), 3—$x = 0.2$ (field parallel to the plane), 4—$x = 0$ (field parallel to the plane).

Figure 7 shows the temperature dependence of the parameter H for antiferromagnets and spin glasses of the $Cd_{1-x}Zn_xCr_2Se_4$ system. This figure shows H_i growing as a function the degree of disorder of the magnet and peaking in the spin glasses. In this case doping, i.e., the magnitude of the magnetocrystalline anisotropy energy, has no substantial effect on the $H_i(T)$ relations. Studies of the temperature dependence of the resonance field in collinear ferromagnets for $x = 0$ and 0.2 have demonstrated that in this case $H_i(T) = 0$.

The relations $H_R(T)$ shown in Fig. 8 are accurately described by the Kittel equations (5) and (6). We can therefore suggest that a resonance field shift of H_i occurs in systems with noncollinear spin ordering and is absent in collinear magnets. The behavior of the ordered spiral AFM $ZnCr_2Se_4$ is therefore analogous to that of spin glasses. This hypothesis is consistent with studies of reentrant ferromagnets. Indeed, the magnetic resonance line shift in reentrant FM's occurs at temperatures rather close to the reentrant

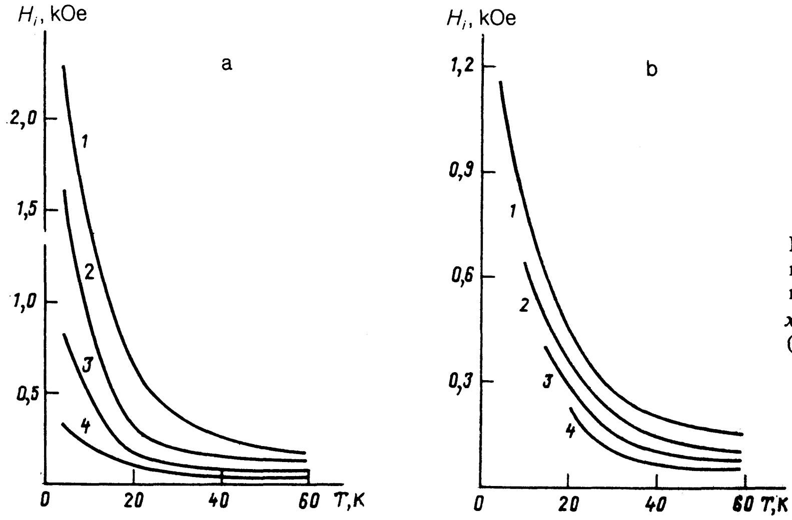

FIG. 7. Temperature dependence of the effective field H_i: a—for reentrant ferromagnets and spin glasses for $x = 0.46$ and 2 mol.% Ag (1); $x = 0.43$ and 2 mol.% Ag (2); $x = 0.38$ (3); $x = 0.35$ and 0.5 mol.% (4); b—for spiral AFM's for $x = 0.43$ (1), 0.46 (2), 0.8 (3), 1.0 (4).

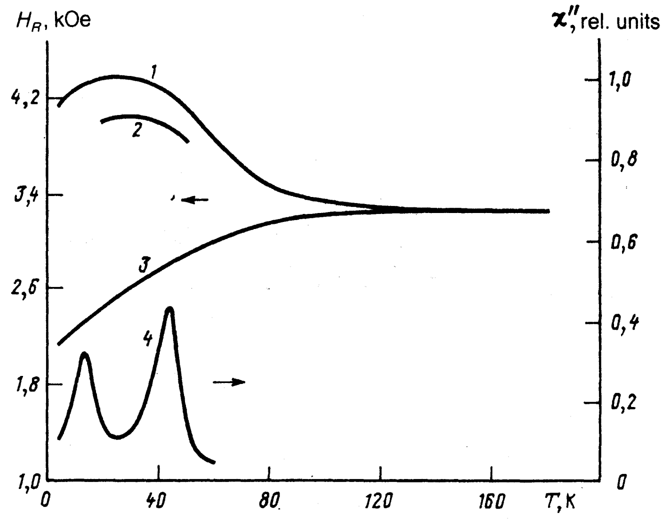

FIG. 9. Temperature dependence of the resonance field magnitude H_R (1, 2, 3) and the imaginary part χ'' (4) of the low-frequency magnetic susceptibility for a reentrant FM with $x = 0.35$ and 0.5 mol.% Ag: 1, 2—external field perpendicular to the wafer plane; 3—field parallel to the plane (curve 2—H_R for the fundamental magnetostatic resonance mode).

transition to the spin glass state, when regions with a chaotically-frozen local magnetization, i.e., short-range noncollinear order, occur in FM's. Figure 9 shows H_R vs. temperature for a reentrant FM. Figure 9 also shows the temperature dependence of the imaginary part χ'' of the low-frequency magnetic susceptibility. The peaks of the temperature dependence of χ'' correspond to the temperatures $T_c = 45$ K and $T_g = 14$ K for transition to the FM state and to the spin glass state, respectively. The relations $H_R(T)$ were found to satisfy the Kittel equations (5) and (6) in the temperature range 80–150 K, with a noticeable resonance field shift of $H_i(T)$ occurring at lower temperatures, as shown in Fig. 7a. Note that the magnetic resonance line shift occurs in SG's and spiral AFM's at temperatures substantially higher than the magnetic transition temperatures T_g and T_N, i.e., still in the paramagnetic range. This phenomenon is therefore related to the onset of short-range noncollinear order in the system, when there are noticeable correlations between neighboring spins.

2.3. Formulation of the phase diagram

We observed magnetic resonance in the AFM samples in our experiments only at temperatures above T_N, excluding the strongly disordered AFM with $x = 0.43$. AFM resonance is not observed below the Néel temperature at relatively low microwave frequencies in the x ray band due to the gap in the elementary excitation spectrum of the antiferromagnet. There is no such gap in spin glasses. We can use this fact in formulating the phase diagram of the system. The magnetic resonance line intensity I drops off in AFM's and SG's with decreasing temperature, while the linewidth grows in this case. As $T \to T^*$ $I \to 0$. In spin glasses we have $T^* < 0$, and in FM's $T^* \approx T_N$.

Figure 10 shows the temperature dependence of the resonance line intensities for SG's and AFM's. The temperatures $T^* \approx T_N$ can be determined by extrapolating the relation $I(T) \to 0$. It would be possible to observe the reentrant manifestation of magnetic resonance at temperatures $\sim T_g$ corresponding to the transition to the spin glass state in reentrant AFM's by further cooling below T_N. We did not detect a reentrant transition at temperatures $T \gg 4.2$ K, even in strongly disordered AFM's at values of x near the concentration range of spin glasses. This transition may lie below 4.2 K, or its absence may be an anomalous property of spiral AFM's. This same result is obtained from measurements of the relations $\chi''(T)$. No low-temperature peak of the relation $\chi''(T)$ is observed even in an AFM with $x = 0.43$. However, magnetic resonance was observed in this sample at temperatures below T_N. The gap in the excitation spectrum of this AFM already appears to be quite small in this case.

Figure 11 shows the phase diagram for the $Cd_{1-x}Zn_xCr_2Se_4$ system plotted from low-frequency magnetic measurements (solid curves). The dashed curves represent the relation $T^*(x) \approx T_N$ plotted from the extrapolation $I(x) \to 0$. The line $T^*(x)$ lies below the line $T_N(x)$, since the gap in the excitation spectrum of the antiferromagnet may be quite small in some temperature range near T_N.

There is one additional method of formulating the phase diagram for reentrant ferromagnets, based on observing the magnetostatic modes excited in the ferromagnetic wafer at temperatures $T_g < T < T_c$. The temperature dependence of H_R for the fundamental magnetostatic mode with **H** perpendicular to the plane of the wafer is shown in Fig. 9.

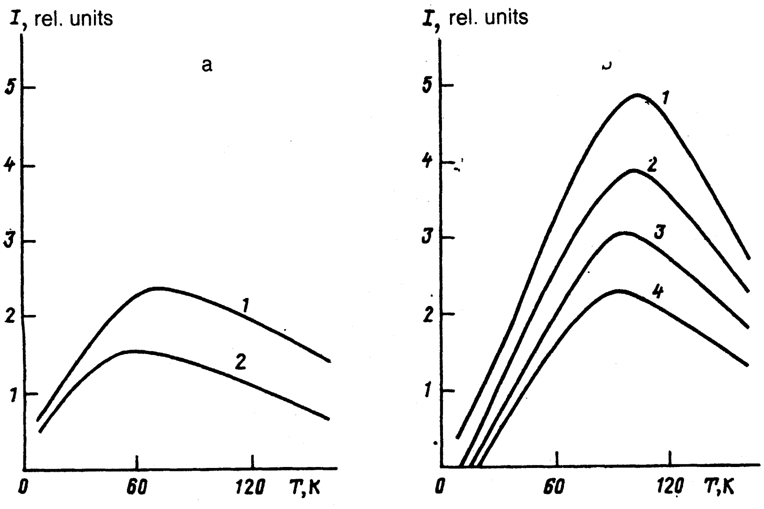

FIG. 10. Temperature dependence of the magnetic resonance line intensity I: a—for spin glasses for $x = 0.46$ and 2 mol.% Ag (1), $x = 0.5$ and 2 mol.% Ag (2); b—for spiral FM's for $x = 0.46$ (1), $x = 0.5$ and 0.5 mol.% Ag (2), $x = 0.52$ (3), $x = 0.8$ (4).

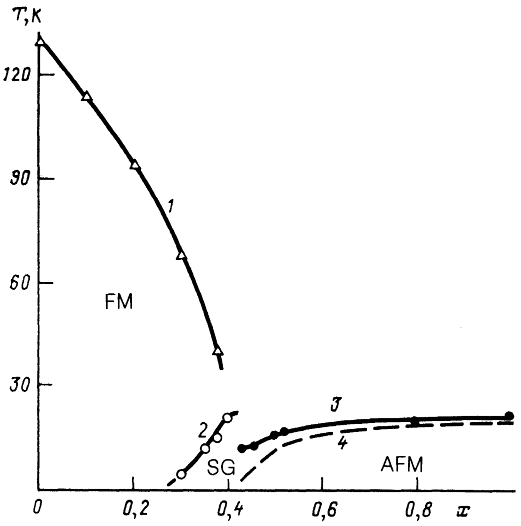

FIG. 11. Phase diagram of the $Cd_{1-x}Zn_xCr_2Se_4$ system: 1—T_c, 2—T_g, 3—T_N, 4—T^*.

The magnetostatic modes vanish as $T \rightarrow T_g$ due to strong damping of spin waves in the disordered magnet, which becomes a ferromagnet upon the return transition to the spin glass state. We observed this phenomenon in different reentrant ferromagnets of the $Cd_{1-x}Zn_xCr_2Se_4$ system.

3. EXPERIMENTAL RESULTS

Research on single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system reveals that the anomalous shift of the magnetic resonance line in spin glasses is due to the noncollinearity of their magnetic structure. The effective internal field H_i is of an exchange nature and is unrelated to the magnetocrystalline anisotropy, the Dzyaloshinskii-Moriya interaction, or the dynamic shift due to dipole broadening. The Cr^{3+} ions are ordered at the octahedral sites of the spinel structure in single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system and therefore form a simple cubic lattice. In this case dipole interactions are not as significant as in spin glasses with a chaotic spin distribution in the lattice.

Inhomogeneous spin precession is excited at magnetic resonance in noncollinear magnets. An effective exchange field acts on each spin under inhomogeneous precession. Such a field may arise at temperatures above the noncollinear magnetic ordering temperature, if short-range magnetic order has been established in the system, i.e., if clusters with a local noncollinear structure are formed. We know that short-range order arises in SG substantially above T_g (Ref. 20). A pulsed stroboscopic analysis has revealed[21] a broad ($\sim T_g$) temperature range above T_g in which clusters of any size may arise in SG of the $Cd_{1-x}Zn_xCr_2Se_4$ system. This will cause a logarithmically slow magnetization relaxation rather than an exponential relaxation to be observed over a broad temperature range above T_g in SG, as is the case in systems with a single characteristic relaxation time. The short-range order is characterized by the correlation function

$$F_{ij}(T, H)=3^{1/2}\langle \hat{s}_i,\ \hat{s}_j\rangle/S(S+1)(2S+1), \tag{11}$$

i.e., the thermodynamic average of the scalar product of the spin operators $\hat{s}_i$ and $\hat{s}_j$ at sites i and j. The function F_{ij} has been shown to be related to the isotropic volume magnetostriction $\Delta V/V$ of the paraprocess.[22] This striction is proportional to the product of F_{ij} and the volume derivative $\partial J_{ij}/\partial V$ of the exchange interaction parameter J_{ij} between spins at nodes i and j. The magnitude of the isotropic volume magnetostriction of the paraprocess for an isotropic magnet is determined, to within a factor of order unity, by the relation

$$\frac{\Delta V}{V} \sim \sum_{i,j} F_{ij}K^{-1}\frac{\partial J_{ij}}{\partial V}, \tag{12}$$

where K is the uniform compression modulus. It is usually sufficient to account for the interaction of nearest and next-nearest neighbors in the sum over i and j. Isotropic volume striction of the paraprocess is therefore determined by local magnetization within a region of a size corresponding to a few lattice constants.

The isotropic volume magnetostriction of the paraprocess in single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system has been demonstrated to be positive[18,19] and equals $\sim 3\cdot 10^{-4}$ for $H \sim 3$ kOe. The crystal volume V grows under magnetization, which leads to an increase in the ferromagnetic exchange interaction energy. One possible mechanism is that the spin glasses of the $Cd_{1-x}Zn_xCr_2Se_4$ system experience local strains under magnetization such that local changes in exchange interactions serve to increase the local magnetization components parallel to the external magnetic field. On the average, the crystal undergoes isotropic bulk extension.

We use the following results to approximate the change in the external field-induced average exchange interaction. We know[23] that the T_c of $CdCr_2Se_4$ samples decreases under isotropic volume compression in proportion to the applied pressure p. The derivative $\partial T_c/\partial p$ in this case is equal to $-0.82\ \text{kbar}^{-1}$, while the uniform compression modulus K is $0.5\cdot 10^6$ bar. We estimate the average change in the volume interaction energy with an average change in volume of $\Delta V/V \sim 3\cdot 10^{-4}$ in fields of ~ 3 kOe in which magnetic resonance is observed. We show in an average field approximation that

$$z\Delta J = 3k_B\left(-\frac{\partial T_c}{\partial p}\right)\frac{\Delta V}{V}\frac{K}{S(S+1)}, \tag{13}$$

where z is the number of effectively interacting neighbors, $S = 3/2$ is the spin of the Cr^{3+} ions, and k_B is Boltzmann's constant. We obtain the estimate $x\Delta J \sim 1.3\cdot 10^{-17}$ erg from Eq. (13). Such a change in the exchange interaction corresponds to a change in the effective exchange field H_{eff} of magnitude

$$\Delta H_{eff} = Mz\Delta J/n(g\mu_B)^2 \approx 0{,}5\ \text{kOe},$$

where $n \sim 10^{22}$ is the concentration of Cr^{3+} ions in the system, μ_B is the Bohr magneton, and the magnetization is $M \approx 150$ Gauss at $H \approx 3$ kOe. The correct order of magnitude for H_i is therefore obtained: $H_i \sim \Delta H_{\text{eff}}$, although in a more exact calculation it is necessary to consider the inhomogeneous crystal strains arising in regions with short-range magnetic order. Such local strains will depend on the external field direction. On the average the crystal undergoes isotropic striction whose magnitude is independent of the field direction.

The question as to why H_i is within an order of magnitude for different spin glasses remains. We use results of a hydrodynamic theory of spin glasses in disordered magnets to answer this question.[24,25] According to this theory, the dispersion law of spin waves in an isotropic Heisenberg SG is

$$(\omega/\gamma)^2=k^2\rho_s/\chi, \tag{14}$$

where $\mathbf{k}$ is the wave vector of the spin wave, ρ_s is the spin rigidity of the magnet, and χ is its magnetic susceptibility. The equation reported in Ref. 24 is used to estimate the spin rigidity ρ_s of the SG's:

$$\rho_s\leqslant V^{-1}\sum_{i,j}r_{ij}{}^2J_{ij}\langle\hat{S}_i,\hat{S}_j\rangle, \tag{15}$$

where r_{ij} is the distance between lattice sites i and j. The modified exchange interactions resulting from magnetostriction strains alter ρ_s according to relation (15). Possibly $\rho_s=0$, holds when we have $\langle J_{ij}\rangle=0$ in unstrained spin glass (for $H=0$). The theoretical results reported by Binder and Young[9] support this conclusion. The equation from Ref. 24 can be used to estimate ρ_s in spin glasses for $H=0$:

$$\langle\omega_{\mathbf{k}}{}^2\rangle=\int_{-\infty}^{\infty}\omega\chi''(\mathbf{k},\omega)d\omega\Big/\int_{-\infty}^{\infty}\omega^{-1}\chi''(\mathbf{k},\omega)d\omega, \tag{16}$$

where χ'' is the imaginary part of the dynamical magnetic susceptibility. We know that $\chi''(\omega)$ vanishes as $\omega\to0$ in SG for $T\leqslant T_g$, and remains virtually constant at low frequencies.[9] Consequently, the integral in the denominator of relation (16) diverges logarithmically at zero. It follows from relations (14) and (16) that

$$k^2\rho_s=\chi\langle\omega_k{}^2\rangle/\gamma^2=0,$$

i.e., the gap in the excitation spectrum of the SG is equal to zero even for $k\neq0$. The spin glass undergoes an isotropic volume striction $\Delta V/V$ when magnetic resonance is observed in a magnetic field $H=H_R$. This shifts the exchange interactions by $\Delta V(\partial J_{ij}/\partial V)$. A finite rigidity $\rho_s\neq0$ arises in the system. A dispersion law has been derived[24,25] for spin-wave modes polarized perpendicular to the magnetization vector $\mathbf{M}$:

$$\omega/\gamma=\rho_{s\perp}k^2/M, \tag{17}$$

where $\rho_{s\perp}$ is the spin rigidity for spin-wave modes polarized perpendicular to the magnetization vector. If the spin rigidity goes from zero to $\Delta\rho_s$ upon application of magnetic field H_R, the magnetic resonance for radiation of frequency ω will be observed for $H_R=\omega/\gamma-\Delta\omega/\gamma$, where

$$\Delta\omega/\gamma=\langle k^2\Delta\rho_s/M\rangle_{\mathbf{k}}$$

is the average over all $\mathbf{k}$ where the spin-wave modes interact efficiently with the microwave radiation. Microwave radiation excites spin waves with $\mathbf{k}=\pm\mathbf{q}$ in a spiral AFM with a spiral propagation vector $\mathbf{q}$, as demonstrated in Ref. 26. In a spin glass, the spin directions change randomly from site to site in the crystal. We denote by L the average distance over which the local magnetization reverses direction. L will be of the order of the lattice parameter in concentrated and rather homogeneous SG. Microwave radiation excites a broad spin-wave packet with different k, where $\langle k\rangle\sim L^{-1}$ in spin glasses. Using Eqs. (15) and (17), we obtain an estimate for $H_i=\Delta\omega/\gamma$:

$$H_i\sim\left\langle M^{-1}k^2\sum_{i,j}r_{ij}{}^2\langle\hat{S}_i,\hat{S}_j\rangle\frac{\partial J_{ij}}{\partial V}\frac{\Delta V}{V}\right\rangle_{\mathbf{k}}. \tag{18}$$

We obtain from relations (12) and (18) for $\langle k\rangle\sim L^{-1}$

$$H_i\sim\beta M^{-1}K(\Delta V/V)^2, \tag{19}$$

where β is a parameter characterizing the degree of noncollinearity of the magnet spins. Spin waves of a wavelength of the order of the interatomic distances are efficiently excited for $L\sim a$. Ordinarily it is sufficient to carry out summation in relation (18) over the first and second coordination shells. Hence, from Eq. (18) after summation and averaging over the vectors $\mathbf{k}$ we obtain relation (19) with the coefficient $\beta\sim1$. For $L\gg a$ we have $\beta\ll1$. This case may occur in inhomogeneous, cluster spin glasses. We note that $K(\Delta V/V)^2$ is the squared elastic energy density of the spin glass related to magnetostriction stresses resulting form the application of field H_R. If this energy density is of order MH_R, we then obtain from relation (19)

$$H_i\sim\beta H_R. \tag{20}$$

This appears to be valid for disordered magnets with competing ferromagnetic and antiferromagnetic interactions, when the volume average satisfies $\langle J_{ij}\rangle=0$ for $H=0$. Indeed, if the number of frustrated spins is of the order of the total number of spins in the system, a relatively small stresses suffice to produce noticeable FM pairing of these frustrated spins with their neighboring spins. We can therefore expect that the corresponding increase in magnetization ΔM due to magnetostriction will be $\sim M(H)$. This explains why the resonance field shift in different spin glasses is comparable in magnitude to the resonance field H_R itself and is essentially independent of the spin glass parameters.

4. CONCLUSION

It has been established from studies of magnetic resonance in single crystals of the $Cd_{1-x}Zn_xCr_2Se_4$ system that the anomalous shift of the magnetic resonance line in spin glasses can be attributed to the noncollinearity of the spins in these disordered magnets. The effective internal field H_i is demonstrated to have an exchange character, and the magnitude of this field is found to be unrelated to the magnetocrystalline anisotropy energy level, the Dzyaloshinskii-Moriya interaction, or the dynamic shift due to dipole broadening. A method of formulating a phase diagram for reentrant disordered magnets is proposed. In the case of reentrant AFM's the method is based on observing a gap in the excitation spectrum of the antiferromagnets (there is no such gap in the excitation spectrum of spin glasses). In the case of reentrant FM's, the method is based on observing magnetostriction modes excited in an FM wafer at temperatures above T_g that are not excited in spin glasses.

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