Photoinduced increase in the magnetization in the region of a phase transition in the ferromagnetic semiconductors $CdCr_2Se_4$ and $HgCr_2Se_4$

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An investigation has been made of the influence of pulses from an optical parametric oscillator ($\tau \approx 15$ ns, $\lambda = 0.66$–$2.7\,\mu$m) on the magnetization of magnetic semiconductors $CdCr_2Se_4$ and $HgCr_2Se_4$ containing small amounts of Ga. At temperatures $T \geqslant T_C$ in an external magnetic field up to 6 kOe the light pulses from the parametric oscillator emitting at a wavelength close to the fundamental optical edge of these materials enhanced the magnetization. The photoinduced increase in the magnetization was due to enhancement of the exchange interaction of magnetic ions via photoexcited electrons localized near Ga impurity atoms. An increase in the magnetization by a light pulse with energy density of order 10^{-2} J/cm^2 reached 6 G, corresponding to a shift of the Curie point by ~ 1 K in the direction of higher temperatures.

INTRODUCTION

The possibility of enhancing the exchange interaction (increasing the Curie temperature T_C) in magnetic semiconductors under the influence of light was first considered in Ref. 1. A detailed theoretical investigation of the influence of light on magnetic phase transitions in magnetic semiconductors was reported in Ref. 2. A model considered there postulates an increase in T_C through enhancement of the indirect exchange between magnetic ions due to photoexcited carriers (photoelectrons). According to the estimates, the photoelectron density necessary to shift T_C by 1 K should be on the order of 10^{19} cm^{-3}. The interacting light would have to be very intense in order to reach such high densities of free electrons, which would unavoidably result in strong heating of the material, making it extremely difficult to observe the expected effect.

In the case of magnetic semiconductors this effect has not been observed so far, with the possible exception of the ferromagnetic semiconductor EuS (Ref. 3). However, the exchange enhancement is not only possible because of conduction-band photoelectrons, but also because of photoelectrons captured by defects (including impurity atoms).[4] This situation is more favorable for experimental observation of the photoinduced change in the Curie point because the lifetime of an electron in an energy level of a defect may be much longer than in the conduction band and it should be possible to establish a high density of photoelectrons and defects at fairly low light intensities.

In the case of magnetic semiconductors and insulators containing defects it has been found that light influences different magnetic characteristics such as the magnetic anisotropy, coercive force, magnetic permeability, etc.[5–8] The present paper describes an investigation of the influence of light on phase transitions in magnetic semiconductors containing defects. The investigation was carried out on ferromagnetics $CdCr_2Se_4$ and $HgCr_2Se_4$ with the Curie points 129 and 105 K, respectively.

EXPERIMENTAL METHOD

One of the direct methods for the investigation of the influence of light on phase transitions in magnetic materials is based on measurement of the magnetization component collinear with an external magnetic field. The change in the magnetization under the influence of light pulses is recorded using a measuring coil with its axis parallel to the magnetic field. Such an induction method is preferable to the magnetooptic approach, because the latter can give rise to parasitic effects within the fundamental or impurity absorption bands of the material.[9]

A similar method was used in Ref. 10 to observe an increase in the magnetization of $CdCr_2Se_4$ in the region of T_C under the influence of light pulses from a neodymium laser ($\lambda = 1.064\,\mu$m, $\tau = 20$ ns). However, since the absorption band shifted with increasing temperature toward higher energies and the laser wavelength was within the transparency region of a crystal at temperatures $T > 130$ K, this effect was not investigated over a wide range of temperatures. We used a frequency-tunable source of light. The magnetization measurement method was again of the induction type.

Single crystals were cut into samples in the form of a disk 1–2 mm in diameter and 30–200 μm thick. A measuring coil of 7–10 turns was wound directly on a cylindrical sample. This sample was subjected to a static magnetic field perpendicular to its plane surface and illuminated with light from a pulsed source. The amplitude of the emf induced in the measuring coil was proportional to the rate of change of the magnetic flux and was recorded with an automatic plotter using a pulsed lock-in detector. The light beam, the coil axis, and the magnetic field were all collinear.

Our source was an optical parametric oscillator. It was selected because of the following requirements which had to be satisfied by a laser light source suitable for the investigation of photoinduced phase transitions. Firstly, the power of the light pulses had to be sufficiently high to ensure the necessary photocarrier density. Secondly, the duration of the pulses should be less than the characteristic photoelectron relaxation times and the characteristic time constants of the thermal processes. Thirdly, the source should be spectrally selective and should have a wide spectral tuning range.

We used a barium sodium niobate parametric oscillator which satisfied these requirements.[11] The parameters of the radiation supplied by this oscillator were as follows: the

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pulse length was 15–20 ns; the average energy density of the light incident on a sample was 0.02 J/cm^2; the tuning range was 0.66–2.7 μm; the width of the line emitted within the 1.03–1.1 μm range was less than 20 nm, whereas in the $\lambda < 0.9$ and $\lambda > 1.3$ μm ranges it was less than 1 nm.

The photoinduced change ΔM in the magnetization, proportional to the area under an emf pulse recorded using the measuring coil, was estimated (on the assumption that the emf pulse could be regarded as approximately triangular) from

$$\Delta M,\ \mathrm{G} = \frac{1}{4\pi nSk}\int_0^\tau \frac{d\Psi}{dt}\,dt \approx \frac{1}{4\pi nSk}\left(\frac{d\Psi}{dt}\right)_{max}\frac{\tau}{2} = -\frac{10^4 e\tau}{8\pi nSk},$$

where $k = \min(1,\ 1/\alpha d)$ is the "optical filling" coefficient; d is the thickness of the sample; α is the absorption coefficient; e is the amplitude of the pulse across the measuring coil; $d\Psi/dt$ is the rate of change of the magnetic flux; n is the number of turns in the measuring coil; τ is the pulse duration; S is the disk area.

RESULTS OF MEASUREMENTS AND DISCUSSION

We investigated $CdCr_2Se_4$ and $HgCr_2Se_4$ samples doped with gallium as well as undoped samples. For the gallium-doped samples a photoinduced increase in the magnetization was observed at temperatures above the Curie point. Typical oscillograms of these signals obtained from the measuring coil are shown in Fig. 1. The positive polarity of the signal corresponded to an increase in the magnetization. This positive signal was attained only in a limited range of wavelengths of the incident light. The spectrum of this signal for a sample of $CdCr_2Se_4$:Ga (0.1 at.%) is shown in Fig. 2a. In the region of the spectral maximum (1.25 eV) the signal had the form shown in Fig. 1a, i.e., it repeated the laser pulse profile. The unipolarity of the signal indicated that the relaxation time of the magnetization to the dark value was relatively long (compared with the length of the laser pulses obtained from the parametric oscillator). When the wavelength of the incident light exceeded 1.01 μm, the signal was only negative and this indicated a reduction in the magnetization under the influence of illumination (Fig. 1c). This signal was characterized by leading, and particularly by trailing, edges of greater duration than the signal in Fig. 1a; this was clearly due to the thermal effect of illumination.

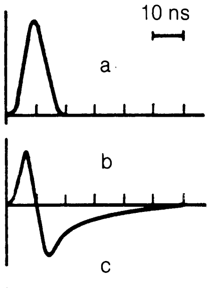

FIG. 1. Profiles of the pulses recorded using a measuring coil: a), b), c) $CdCr_2Se_4$:Ga, $T = 140$ K, $H = 5$ kOe; d), e) $HgCr_2Se$:Ga, $T = 130$ K, $H = 5$ kOe. Photon energy: a) 1.22 eV; b) 1.31 eV; c) 1.02 eV; d) 0.7 eV; e) 0.54 eV.

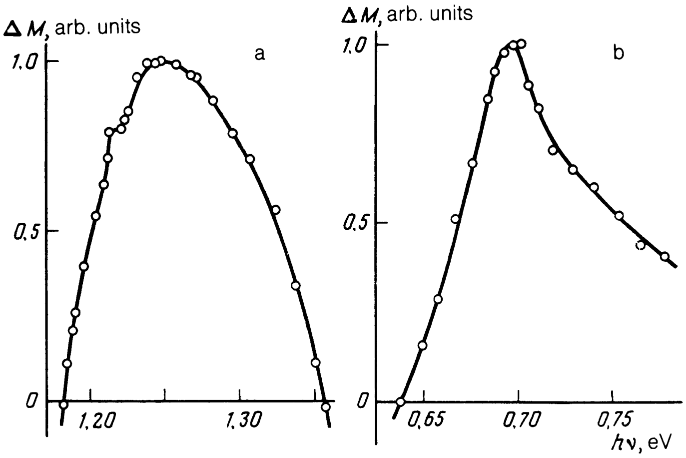

FIG. 2. Spectrum representing the photoinduced change in the magnetization in a field $H = 5$ kOe: a) $CdCr_2Se_4$:Ga (0.1 at.%), $T = 140$ K; b) $HgCr_2Se_4$:Ga (0.5 at.%), $T = 130$ K.

The signal in Fig. 1b was due to the superposition of the competing signals of the type shown in Figs. 1a and 1c when the intensity of illumination was sufficiently high at the short-wavelength edge of the spectrum. The positive signal had the profile shown in Fig. 1a and its amplitude increased proportionally to the intensity of the incident light as long as the energy density per pulse was less than 10^{-2} J/cm^2. A further increase in the light intensity slowed down the rise of the amplitude of the positive signal and distorted its profiles; the positive signal then began to decrease and it was followed by a signal of negative amplitude, which increased approximately proportionally to the intensity of light. Suppression of the photoinduced magnetization by the thermal signal with increasing light intensity occurred as a result of saturation related to the filling of the defect levels with photoelectrons. This was supported, in particular, by the fact that in the case of samples with lower gallium concentrations (0.01 at.%) the amplitude of the positive signal was approximately an order of magnitude less and its suppression by the thermal signal occurred at much lower light intensities.

In the case of the gallium-doped $HgCr_2Se_4$ samples we also observed signals of the type shown in Figs. 1d and 1e. The signal shown in Fig. 1a was not observed for this compound. This clearly suggested that the relaxation time of the magnetization to the dark value obtained for these samples was comparable with the length of the laser pulses. This was supported also by the profile of the signal shown in Fig. 1d, which was close to the derivative of the laser pulse. By analogy with $CdCr_2Se_4$:Ga, the positive signal obtained for $HgCr_2Se_4$:Ga increased as a function of the gallium concentration. The spectrum of the positive component of the sig-

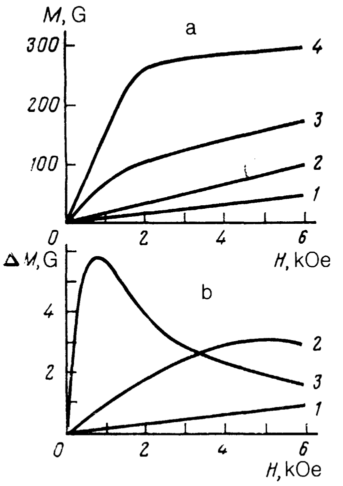

FIG. 3. Field dependence of the magnetization (a) and photoinduced changes in the magnetization (b) obtained for $CdCr_2Se_4$:Ga (0.1 at.%) at the photon energy $h\nu = 1.22$ eV at temperatures (K): 1) 151; 2) 140; 3) 130; 4) 78.

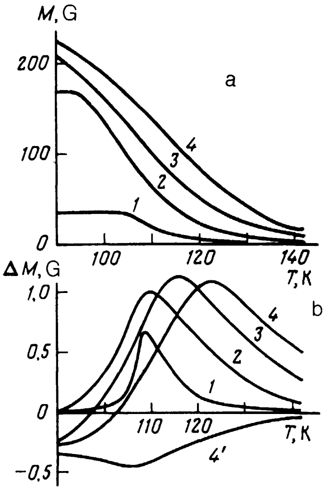

FIG. 5. Temperature dependence of the magnetization (a) and of the photoinduced change in the magnetization (b) obtained for $HgCr_2Se_4$:Ga (0.5 at.%): 1) $H = 0.2$ kOe; 2) 1 kOe; 3) 2.6 kOe; 4), 4') 5 kOe. Photon energy: 1)–4) 0.74 eV; 4') 0.54 eV.

nal in Fig. 1d is shown in Fig. 2b. At incident wavelengths in excess of 1.96 μm the signal was negative and of the form shown in Fig. 1e; this was due to the thermal effect of illumination. The maximum of the spectral dependence of the photoinduced increase in the magnetization of $CdCr_2Se_4$ and $HgCr_2Se_4$ was located near the optical absorption edge of these two materials. Consequently, we can assume that the observed increase in the magnetization was due to electron transitions to impurity levels formed as a result of doping with gallium and located near the bottom of the conduction band, particularly as the effect was not observed in undoped materials.

Figure 3b shows the dependence of ΔM on the external magnetic field H applied to a sample of $CdCr_2Se_4$:Ga (0.1 at.%), recorded at different temperatures. Figure 3a shows the magnetization curves $M(H)$ of the same sample recorded along the [100] direction employing a vibrating magnetometer. The temperature dependences $\Delta M(T)$ and $M(T)$ are plotted for the sample in Fig. 4. Clearly, the dependence $\Delta M(T)$ for the negative signal (when the wavelength was within the transparency range of the sample; see curve 4') resembled the dependence $\partial M(T)/\partial T$. This was further evidence of the thermal nature of the negative signal.

Figures 5 and 6 give the field and temperature dependences of ΔM and M for a sample of $HgCr_2Se_4$:Ga (0.5 at.%). A comparison with the corresponding dependence for $CdCr_2Se_4$:Ga (Figs. 3 and 4) revealed a certain similarity, indicating an analogy in the nature of the processes. The main difference was that in weak fields and at temperatures close to T_C the photoinduced increase in the magnetization was not as great as in the case of $CdCr_2Se_4$:Ga and the corresponding maxima of the curves were much wider. However, in the case of strong fields and at high temperatures the results were very similar. Moreover, the $M(T)$ curve obtained in a weak field (0.2 kOe) did not have a characteristic kink in the region of T_C (which was exhibited by the corresponding curve of $CdCr_2Se_4$:Ga). Hence, we concluded that the phase transition in $HgCr_2Se_4$:Ga (0.5 at.%) was smeared

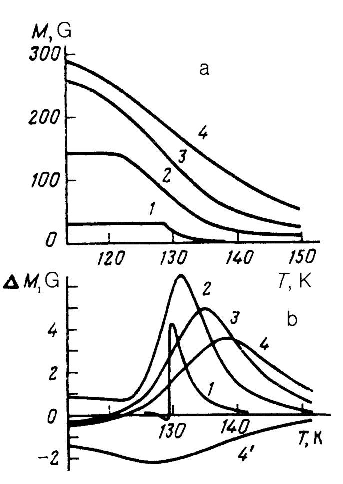

FIG. 4. Temperature dependence of the magnetization (a) and of the photoinduced change in the magnetization (b) of $CdCr_2Se_4$:Ga (0.1 at.%) in the following magnetic fields (kOe): 1) 0.2; 2) 1; 3) 3; 4), 4') 6. The photon energy was as follows: 1)–4) 1.22 eV; 4') 1.01 eV.

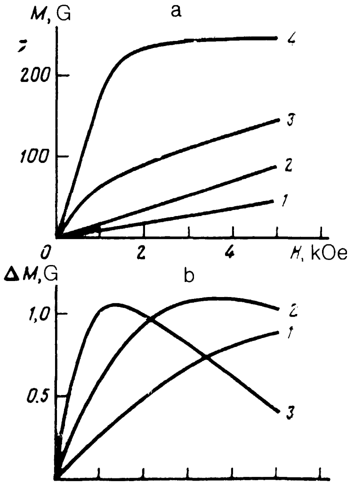

FIG. 6. Field dependence of the magnetization (a) and of the photoinduced change in the magnetization (b) of $HgCr_2Se_4$:Ga (0.5 at.%) at $h\nu = 0.74$ eV at the following temperatures (K): 1) 130; 2) 120; 3) 110; 4) 78.

out. This could be due to an inhomogeneous distribution of the impurity in the bulk of the sample and also a higher concentration of defects than in $CdCr_2Se_4$.

We identified the part of the sample participating in the photoinduced increase in the magnetization (in the region of the spectral maximum) by determining this effect using samples of smaller thickness. We established that the reduction in the thickness of the sample from 200 to 30 μm did not alter the signal amplitude and could lead to an increase in the magnetization under the influence of light (to within 20%). Hence, we concluded that the contribution made to the increase in the magnetization came from a layer of thickness less than 30 μm, i.e., a thickness of order α^{-1}, where α is the absorption coefficient of light ($\alpha \sim 10^3$ cm^{-1}).

The results obtained were described satisfactorily by the following phenomenological model: the interaction of light of wavelength close to the fundamental absorption edge of the material induced electron transitions from the valence band to local levels of defects located near the bottom of the conduction band and associated with the gallium impurity. The electrons became localized at defects and created, by the indirect exchange mechanism, a ferromagnetic ordering of a stronger defect than in the bulk of the crystal. Cooling and approach to the Curie point induced initially the ferromagnetic photoordering in individual isolated regions adjoining the photoinduced centers and the dimensions of these regions were governed by the radius within which an electron was localized at a defect. In the direct vicinity of the Curie temperature the dimensions of the photoinduced ferromagnetic clusters were governed by the spin–spin correlation radius. When the cluster dimensions became comparable with the distance between them (when they began to overlap), the whole of the sample was converted to the ferromagnetic state.

We were able to determine the shift of the Curie temperature knowing the photoinduced change in the magnetization and the nature of the temperature dependence of the longitudinal magnetization of a sample subjected to a fixed external magnetic field.

These estimates could be made most accurately from the temperature dependences of M and ΔM in weak fields (Fig. 4). In these fields the dependence $M(T)$ had a horizontal region due to the presence of a domain structure. In the range $H < 4\pi D M_s(T)$ [where D is the demagnetization factor and $M_s(T)$ is the spontaneous magnetization] the longitudinal magnetization was governed only by the demagnetization factor, $M = H/4\pi D$, and it was independent of T. At a certain temperature when $H = 4\pi D M_s(T)$ a phase transition took place from a polydomain to a single-domain state[12,13] and the $M(T)$ curves had a kink (Fig. 4). In an external magnetic field $H = 0.2$ kOe the photoinduced change in the magnetization was $\sim$4G, which amounted to 20% of the magnetization of the sample. This corresponded to a shift of the kink of the magnetization toward higher temperatures by ~ 1 K. An estimate of the concentration of the photoinduced centers created by incident light of energy density 10^{-2} J/cm^2 gave $\leqslant 2\times10^{19}$ cm^{-3}.

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