Photoinduced phase transitions in magnets

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A theory of photoinduced order-disorder and order-order phase transitions is developed wherein these transitions are treated as cooperative phenomena in open systems. The situation considered is one in which the photoinduced increase in T_c is due to the appearance of nonequilibrium carriers at traps. They unite the spins of the atoms near the traps into magnetic clusters. The effect arises because the spin polarization of the clusters is higher than that of the regular atoms of the crystal. In the mean field approximation the photoinduced second order transition is accompanied by discontinuities in the derivatives of the rate of entropy production and the carrier density with respect to temperature and with respect to the frequency and intensity of the light. An order-order transition can occur because of the accumulation of magnetic Frenkel excitons, forming regions of an altered magnetic phase. The accumulation of excitons is due to their mutual attraction and to the onset of a coherent excitonic state in which the exciton lifetime increases as the region of the excitonic phase grows in size.

1. INTRODUCTION

There are various mechanisms by which light affects the properties of magnets. In particular, circularly polarized light gives rise to a magnetization in a crystal because the photons transfer their angular momentum to the electrons, aligning their spins in a definite direction. Unpolarized light cannot, in and of itself, magnetize a crystal, but it can do so indirectly by changing the exchange interaction or the anisotropy in a magnet. Of particular interest is the situation in which the light causes order-disorder or order-order phase transitions.

A feature of photoinduced phase transitions is that they occur under thermodynamically nonequilibrium conditions. Therefore, they cannot be characterized by anomalies in the derivatives of the thermodynamic potential, and the well-developed theory of thermodynamically equilibrium phase transitions does not apply to them. Photoinduced phase transitions are actually an example of self-organization in nonequilibrium systems.

One can speak of two main types of photoinduced phase transitions—proper and improper. The first type, in which light alters the characteristics of the transition, can also occur in darkness. Light shifts the point of the order-disorder transition and can even convert it from continuous to discontinuous.

If the temperature can be assumed constant throughout the sample, then the rate of entropy production $\dot{S}$ plays a role in nonequilibrium phase transitions that is analogous to the role of the entropy S in equilibrium transitions. Specifically, it turns out that at discontinuous phase transitions it is $\dot{S}$ itself that is discontinuous, while at continuous transitions the anomalous quantities are its derivatives with respect to temperature and with respect to the parameters of the subsystem whose energy is being converted into heat, i.e., with respect to the intensity and frequency of the light. This conclusion was first reached[1] on the basis of a model calculation done on the assumption that the increase in T_c is caused by a superexchange between magnetic atoms due to photoexcited

current carriers. To get a noticeable effect it is necessary to have giant photoelectron densities, of the order of 10^{18} cm^{-3}, and there is as yet no experimental proof that such densities are possible in magnetic semiconductors.

In the present paper we study a new and apparently more realistic mechanism for photoinduced magnetism, involving nonequilibrium current carriers trapped by defects. Normally the number of photoelectrons trapped by defects in photoconductors can be several orders of magnitude larger than the number of free photoelectrons. This effect is particularly pronounced in semiconductors, where there are many attachment centers that trap carriers of only one sign. Until they return to the conduction or valence band, the trapped electrons or holes cannot migrate to a recombination center and vanish. At low temperatures, the possibility that they will be ejected back into the band is small. Therefore, the occupancy of the attachment centers can be very high.

Electrons at local centers influence the magnetic ordering of the crystal in two ways. First, because of the electron-phonon interaction they cause a uniform deformation of the crystal, which is manifested in a change of the lattice constant. The change in the lattice constant in turn causes a change in the exchange integral between magnetic atoms throughout the crystal. A simple calculation shows that the relative increase in the Curie temperature due to the lattice deformation is

$$t = \frac{a}{J_0} \left| \frac{dJ_0}{da} \right| \frac{CNa^3}{3\mu v^2},$$

where J_0 is the exchange integral, a is the lattice constant, C is the interaction constant of the electrons with acoustic phonons (the deformation potential), μ is the mass of the unit cell, v is the speed of sound in the crystal, and N is the concentration of photoinduced defects. Assuming the values $\mu = 10^{-22}$ g, $v = 10^5$ cm/sec, $C = 10$ eV, $a = 3 \cdot 10^{-8}$ cm, and $(a/J_0)|dJ_0/da| = 10$, we obtain for $N = 10^{19}$ cm^{-3} the estimate $t \approx 0.01$ (the radius of the electron orbit is assumed to be so small that no impurity band is formed). Thus we see

that this effect is amenable to experimental observation.

Even more important, however, is the increase in T_c due to the second cause: the influence of the magnetic moments of the defects on the magnetic ordering of the crystal. This effect can be understood qualitatively as follows. A conduction electron trapped by a defect brings about a superexchange in its surroundings, uniting the moments of the atoms over which it is spread into a single defect moment. We assume that the superexchange through an electron within a cluster is much stronger than the direct exchange between magnetic atoms (the temperature T_g at which the cluster is destroyed is much higher than T_c). Then the role of the electron reduces to keeping the moment of the cluster fixed in magnitude, with only its direction in space allowed to vary. If all the defect moments were oriented in the same direction (polarized defects) at all temperatures, no phase transition at all could occur in the system.[2] In fact, the effect of the defects in this case is equivalent to the effect of an external magnetic field on the crystal.

In the case under consideration here, the degree of polarization of the defects goes to zero at the Curie point. Below this point, however, it is substantially higher than the degree of polarization of the regular atoms, and consequently, by analogy with the case of polarized defects, there is a rise in the Curie point T_c of the entire crystal. The reason why the degree of polarization of the defects is higher than that of regular atoms is that the molecular field acting at the defects is approximately the same as at the regular atoms, but the moment of the defect is much larger than that of these atoms. For example, if the defect consists of a central atom and z nearest neighbors, then the defect moment $\mathscr{L}$ is equal to $(z + 1)S$ (S is the magnitude of the spin of the atoms of the crystal), and the interaction energy of such a defect with the regular atoms surrounding it in the nearest-neighbor approximation is $E_D = -z(z - 1)J\overline{M}l^z$, where J is the exchange integral, $l^z = \mathscr{L}^z/(z + 1)$ is the projection of the defect moment (per atom of the defect) onto the magnetization axis Z, and M is the average spin of the regular atoms interacting with the defect (in the expression for E_D we have taken into account that each of the z atoms around the defect interacts with $z - 1$ regular atoms). The expression for E_D can be put in the form $E_D = -H_D\mathscr{L}^z$, where $H_D = J\overline{M}z(z - 1)/(z + 1)$. For $z \gg 1$ the field H_D in the zeroth approximation in $1/z$ is the same as the molecular field $H_m = J\overline{M}z$ acting on the regular atoms of the crystal (actually the ratio H_D/H_m is still larger, since the magnetization of the regular atoms surrounding a defect is higher than that of the atoms far from the defect). The defect moment is $z + 1$ times larger than the spin of a regular atom, and so the degree of polarization of a defect, equal to $\mathscr{L}^z/\mathscr{L}$, is much larger than the degree of polarization $\overline{M}/S$ of the regular atoms. Moreover, this mechanism of photoinduced magnetism gives qualitatively the same anomalies in the rate of entropy production at the transition point as does the mechanism of superexchange through photoelectrons.

The second type of transition is when light puts the crystal in a state that is inaccessible under thermodynamically equilibrium conditions. Such a transition is realized when the light generates long-lived nonmagnetic elementary excitations which join together into droplets of rather large size (e.g., Frenkel excitons at magnetic atoms). The magnetic properties of such regions can differ substantially from those of the unexcited crystal. The magnetic phase transition that occurs under illumination in this case is "improper." It is brought on by the appearance of mutually interacting elementary excitations in the system.

After the light is turned off, the crystal that it has excited is generally not in a metastable state, since its state does not correspond to even a relative minimum of the thermodynamic potential. Nevertheless, the elementary excitations can turn out to be frozen for purely kinetic reasons, and then the magnetic structure arising under illumination can persist for a rather long time. In particular, as we shall show, the Frenkel excitons in the droplets can have an anomalously long lifetime because of the coherence of their states. Specifically, the exciton lifetime in respect to multiphonon transitions increases exponentially with increasing number of atoms in the droplet.

The experimental data on the photoinduced phase transitions agree with the above ideas concerning the two types of transitions. The photoinduced increase in the magnetization was first observed[3] in the ferromagnetic semiconductor EuS. Pulsed laser illumination of a crystal was found to give a photoinduced increase in the Curie temperature of ~ 0.1 K, or $\sim 1\%$. According to the classification proposed above, this is a proper photoinduced transition.

A growth in the magnetization under relatively low-intensity illumination has also been observed[4] in the ferromagnetic semiconductor $CdCr_2Se_4$. The measurements were made at a temperature of 43 K, substantially lower than T_c (130 K). The change in the magnetization corresponded to a shift in T_c by 5 K.

In both of those papers[3,4] it was assumed that the effect is due to superexchange through photoelectrons, but the photoconductivity itself was not measured. However, since it is very difficult to achieve the gaint (in fact, prebreakdown) densities of photoelectrons necessary for such shifts in T_c, it is more likely that the shift in T_c here is due to photoelectrons trapped by defects, and the theory developed in the present paper gives a more satisfactory explanation of the results of Refs. 3 and 4. The anomalies in the rate of entropy production and in the density of photoelectrons have not been studied experimentally.

Another example of a proper transition is the photoinduced spin-reorientation observed in $ErCrO_3$ at temperatures below the point at which this transition occurs in darkness.[5] As to improper phase transitions, one such transition has apparently been observed[6] in the antiferromagnetic insulator $EuCrO_3$. Laser illumination of this magnet led to a change in the antiferromagnetic resonance spectrum, with a threshold in the pump power and duration. It was assumed[6] that the illumination caused the crystal to go from a metastable state to the true ground state. However, if that were the case, the ground state could also be reached by other means, such as a very slow cooling. This was not seen in the experiment. It seems entirely justified to assume that Frenkel excitons arising at the Eu^{2+} ions coalesce into droplets having a very long lifetime. If the pump power is insufficiently high,

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the excitons will not manage to coalesce into long-lived droplets during their relatively short lifetime and will therefore annihilate.

2. MODEL FOR PROPER PHOTOINDUCED PHASE TRANSITIONS

In this section we shall assume that light illuminating a ferromagnetic semiconductor excites photoelectrons which then accumulate at attachment levels. After making the transition to an attachment level, a photoelectron causes a ferromagnetic coupling between the atoms in its vicinity.[7] We assume that this coupling is so strong that the moments of all these atoms for $T \lesssim T_c$ are bound into a single cluster characterized by a total moment. Further, since the lifetime of an electron at an attachment level is known to be large compared to the time required to establish thermodynamic equilibrium in the spin subsystem for a given number of occupied attachment levels, the moments of the clusters are found in thermodynamic equilibrium with the moments of the regular atoms. The electrons in the conduction band, on the other hand, can have a lifetime in the band that is comparable to the time required for the establishment of equilibrium among the spins of the regular atoms, and they can therefore have a substantially nonequilibrium moment.

Let us start with the description of free electrons. We assume that the width W of their conduction band is large compared to the energy AS of their exchange interaction with the localized spins, where A is the s-f exchange integral and S is the magnitude of the f spin. The character of the energy spectrum of a conduction electron near T_c depends substantially on the radius r_0 of the exchange interaction between f spins. The spin correlation of neighboring atoms is proportional to r_0^{-2}. If r_0 is small, then these correlations are large, and the spins of the long-wavelength conduction electrons have a substantial tendency to align with the local moment of the crystal. Thus these spins do not have a definite direction in space, but fluctuate together with the local moment of the crystal.[7] On the other hand, if the exchange radius is large, then the correlators are small, and the alignment of the electron spin to the local moment is not important. We can therefore assume that the projection σ of the electron spin is fixed. This can be seen from that fact that for large r_0 we obtain a small value for the imaginary part of the mass operator of an electron with quasimomentum k and spin projection σ in the Born approximation for $T > T_c$ (Ref. 7):

$$\mathrm{Im}\, M_{k\sigma} \approx (A^2 S^2 / W r_0^2 k) \ln (1 + 4k^2/\varkappa^2),$$

where $\varkappa$ is the inverse correlation radius. In what follows, for the sake of definiteness, we consider the case of large r_0. The case of small r_0 will be the subject of a separate paper, where it will be seen that the results remain qualitatively the same as in the case of large r_0.

In accordance with what we have said, the electron spectrum can be assumed to be given by the simple expression

$$E_{k\sigma} = E_k - A\sigma \overline{M}, \tag{1}$$

where E_k is the electron energy in the absence of s-f exchange. Formula (1) applies near T_c if the characteristic

electron energy is large compared to the energy associated with the alignment of the electron spin with local fluctuations, the latter being given[7] by the expression

$$E_0 \approx (AS)^{4/3} W^{-1/3} (a/r_0)^{4/3}. \tag{2}$$

To describe the state of the conduction electrons, one must know their distribution function. It is natural to assume that the time required for the electrons to diffuse from the level to which they are excited to the bottom of the conduction band is small compared to the time for their capture to local levels. In this case one can assume that all the electrons are concentrated near the bottom of the conduction band. At sufficiently high densities the electrons can be regarded as degenerate. We also assume, as is actually true in the majority of cases, that the holes interact with the localized moments much more weakly than do the electrons. By assumption, there are no attachment levels for holes. Therefore, the holes do not directly influence the magnetization of the crystal.

The kinetic equation that determines the density n_σ of photoelectrons in the conduction band is of the form

$$\frac{dn_\sigma}{dt} = G_\sigma - P(n_\sigma - \bar{n}_\sigma) - \frac{n_\sigma}{\tau_r} - \frac{n_\sigma}{\tau_d}\left(1 - \frac{N}{N_L}\right) + \frac{N}{\tau_u}\left(\frac{1}{2} + \sigma x\right), \tag{3}$$

$$G_\sigma = R(\omega - E_g + A\sigma \overline{M})^{1/2}. \tag{4}$$

Here G_σ is the rate of generation of current carriers by light of frequency ω; R is a coefficient which is proportional to the intensity of the light and depends on the details of the band structure; E_g is the width of the optical gap in the paramagnetic region. The second term in (3) describes the spin relaxation of the photoelectrons. The quantity $\bar{n}_\sigma$ denotes the thermodynamically equilibrium density of photoelectrons with spin projection σ at a given average magnetization $\overline{M}$ of the crystal and a given photoelectron density $n = n_\sigma + n_{-\sigma}$. The term proportional to τ_r^{-1} describes the capture of photoelectrons by recombination centers and their subsequent annihilation. The term proportional to τ_d^{-1} describes the transition of the electron to the attachment level, N_L is the total density of such levels, and N is the density of occupied levels. The last term in (3) describes the inverse transitions from the attachment levels to the conduction band. This expression contains the degree of polarization x of the defect moments because the electron spin at a cluster is directed along the moment of the cluster. If the moment of the cluster makes an angle of γ with the moment of the crystal, then according to the rules for spinor transformations the probability for the transition of an electron from the cluster to a band with spin projection σ is proportional to $1/2 + \sigma\cos\gamma$; after an averaging over all the defects, this gives the corresponding expression in (3).

The times τ_r, τ_d, and τ_u in (3) are all assumed to be independent of the magnetization of the crystal. This makes it possible to write the kinetic equation directly for the total density of electrons at the attachment levels:

$$dN/dt = -N/\tau_u + (n/\tau_d)(1 - N/N_L). \tag{5}$$

In accordance with our above assumption of a rapid relaxation of the spins of the clusters formed around defects occu-

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pied by electrons, we can assume that their moments have a thermodynamically equilibrium spatial distribution.

Equation (3) assumes that the electron density is lower than the density of levels between the bottom of the corresponding subband of the conduction band and the level to which the transition occurs:

$$n_{\omega\sigma} = [2m^*(\omega - E_g + A\sigma\bar{M})]^{3/2}/6\pi^2, \qquad (6)$$

where m^* is the effective mass of the electrons (the effective mass of the holes is assumed to be much larger than that of the electrons). Restriction (6) should be taken into account in analyzing Eqs. (3)–(5).

3. THERMODYNAMIC AND SYNERGETIC POTENTIALS OF A CRYSTAL CONTAINING DEFECTS

The average magnetization M of the crystal is determined by minimizing an expression which has the structure (but not the meaning) of the density of the incomplete thermodynamic potential (the "synergetic" potential)[1]

$$\varphi = \varphi_0 + \varphi_l + \varphi_c,$$

$$\varphi_l = \int_0^{\bar{M}} N(\bar{M}) \frac{df_l}{d\bar{M}} d\bar{M}, \qquad \varphi_c = \sum_\sigma \int_0^{\bar{M}} n_\sigma(\bar{M}) \frac{d\varepsilon_\sigma}{d\bar{M}} d\bar{M}. \qquad (7)$$

Here φ_0 is the density of the incomplete thermodynamic potential of the crystal in the absence of photoexcitation, φ_l and φ_c describe the work performed on the crystal by the trapped and free electrons, respectively, during the establishment of the average magnetization $\bar{M}$; f_l is the change in the free energy of the system upon the appearance of a single trapped electron; ε_σ is the change in the energy of the electron gas upon the appearance of an electron with spin projection σ. Because all the electrons are concentrated near the bottom of the conduction band, we have, according to (1),

$$d\varepsilon_\sigma/d\bar{M} = -A\sigma. \qquad (8)$$

While the sum of the first two terms in (7) can be justified on the basis of equilibrium statistics, the third term is justified by proceeding from the equations of motion for the electron and spin operators with allowance for the interaction of the latter with the constant-temperature bath.[1] If the electrons in the crystal are in thermodynamic equilibrium (a doped semiconductor), expression (7) goes over completely to the thermodynamic potential of the system.

Let us now turn to an evaluation of the defect contribution to the free energy. The influence of polarized defects on the phase transition was studied with the aid of a phenomenological model in Ref. 8. However, the results of Ref. 8 cannot be applied directly to the case under study, since the correspondence between the phenomenological parameters used in that paper and the microscopic parameters of our problem has not been established, and we have therefore been unable to make quantitative estimates of the effect. Furthermore, the model of Ref. 8 is essentially the Ising model, while we are considering an isotropic magnet. Let us therefore do the analogous calculation, but on the basis of the microscopic Heisenberg model.

In the molecular field approximation the influence of a

defect on the spin subsystem of the regular atoms can be described by introducing a defect field conjugate to the order parameter (the magnetization M). The density of this field created at site f by a defect centered at r_i is

$$h_{di}(f) = \frac{1}{a^3} S \cos\gamma_i \sum_{f'} J(f - f') \theta(r_d - |f' - r_i|), \qquad (9)$$

where $J(f - f')$ is the exchange integral for the spins of atoms f and f', γ_i is the angle between the direction of the defect moment and the magnetization axis of the spin subsystem, r_d is the radius of the region in which the defect electron is localized, and $\theta(x)$ is the unit step function.

To study the thermodynamics of a magnet containing defects, let us consider the free energy of the system in the continuum approximation, with allowance for the nonuniform distribution of the magnetization over the volume of the crystal due to the presence of defects:

$$F = \int dV \left[\varphi_0(M) + \frac{g}{2}(\nabla M)^2 - h_d(r)M \right] - \frac{3}{2} T \sum_i \cos^2\gamma_i,$$

$$h_d(r) = \sum_i h_{di}(r), \qquad \varphi_0(M) = \frac{1}{2}\alpha_0\left(\frac{T - T_{c0}}{T_{c0}}\right)M^2 + \frac{1}{4}\beta M^4,$$

$$\alpha_0 = \frac{J_0}{a^3}, \qquad T_{c0} = \frac{J_0 S^2}{3}, \qquad \beta = \frac{3}{5}\frac{J_0}{S^2 a^3}, \qquad J_0 = \sum_f J(f),$$

$$g = \frac{1}{6}r_0^2\frac{J_0}{a^3}, \qquad r_0^2 = \frac{1}{J_0}\sum_f f^2 J(f). \qquad (10)$$

The last term in (10) takes into account the configurational entropy of the defects in the case of classically large defect moments. It is found by summing over all the microscopic states corresponding to a given set of angles γ_i. For brevity, the expressions for the coefficient β and the Curie temperature T_{c0} of the ideal crystal in darkness are given for the case of classically large atomic spins S (the generalization to the quantum case is elementary). The integration in (10) is over the region outside the defects. However, the dimensions of the defects are assumed to be small compared to the distances between them, and in all the subsequent calculations we keep only the terms of leading order in $r_d N^{1/3}$.

Since the case we are considering in this paper is one of defects whose moments can change their direction in space, to determine the equilibrium state of the system we must minimize free energy (10) with respect to both the order parameter M and the spin configurations of the defects specified by the sets of angles γ_i. It is clear on physical grounds that the degree of polarization of the defects is proportional to the magnetization of the regular atoms, and their contribution to free energy (10) is therefore in fact quadratic in M. The defects under consideration here are thus analogous to the "random temperature" defects studied by Lebedev et al.,[9] who found the same defect shift of the transition temperature that is obtained on the assumption that the order parameter is uniform along the sample. Therefore, in minimizing (10) we shall assume that the magnetization $M(r)$ is constant and equal to its volume averaged value $\bar{M}$.

Minimizing (10) with respect to $\bar{M}$, we find

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$$\varphi_0{}'(\overline{M}) = NHx, \qquad x = \frac{1}{NV}\sum_i \cos\gamma_i,$$

$$H = \frac{1}{\cos\gamma_i}\int dV\, h_{di}(r)$$

$$= \sum_{ff'} SJ(f-f')\theta(r_d-|f-r_i|)[1-\theta(r_d-|f'-r_i|)], \qquad (11)$$

where V is the volume of the crystal. The quantity H has the meaning of the energy of the exchange interaction of the defect with a spin subsystem of unit magnetization in the case when the direction of their moments coincide. The parameter x in (11) is obviously the degree of spin polarization of the defects that appears in (3). By minimizing (10) with respect to $\cos\gamma_i$ with allowance for (11), we obtain the steady-state value of this parameter:

$$\cos\gamma_i \equiv x = H\overline{M}/3T. \qquad (12)$$

After substituting (12) into (10), we get an expression for the quantity f_l appearing in (7):

$$f_l(\overline{M}) = -H^2\overline{M}^2/6T. \qquad (13)$$

4. SHIFT OF THE CURIE POINT AND ANOMALIES IN THE RATE OF ENTROPY PRODUCTION

The photoelectron contribution to φ near T_c is an important part of the term $\sim\overline{M}^2$, since the latter goes to zero. However, the photoelectron contribution is not essential to the term $\sim\overline{M}^4$, which retains its normal value near T_c. We shall therefore evaluate the corrections to φ_0 in (7) with allowance only for terms $\sim\overline{M}^2$. From (7), (8), and (13) we easily see that for this we must calculate the density N of localized photoelectrons in the zeroth approximation, while the difference $n_\uparrow - n_\downarrow$ in the densities of free photoelectrons in the subbands must be calculated to first order of $\overline{M}$.

If we treat the gas of free photoelectrons as degenerate, we find from (3)–(5) with allowance for (12)

$$N = N_R = n_R(n_R/N_L + \tau_u/\tau_d)^{-1}, \qquad n_R = 2R\tau_r(\omega - E_g)^{\frac{1}{2}}, \qquad (14)$$

$$n_\uparrow - n_\downarrow = \delta_R = \overline{M}\left[\frac{1}{2}n_R U + \frac{3}{4}AP\tau_r\frac{2m^*n_R}{(3\pi^2 n_R)^{\frac{2}{3}}} + \frac{N_R H}{3T}\frac{\tau_r}{\tau_u}\right]$$

$$\times\left(1 + P\tau_r + \frac{N_R H}{n_R}\frac{\tau_r}{\tau_u}\right)^{-1}, \qquad U = \frac{A}{2(\omega - E_g)}. \qquad (15)$$

The quantity n_R in (14) is equal to the density of free photoelectrons for $\overline{M} = 0$.

Substituting (14) and (15) into (7), taking (8) and (13) into account, and considering the explicit form (10) of the function $\varphi_0(M)$, we can write the synergetic potential density as a function of $\overline{M}$:

$$\varphi(\overline{M}) = \frac{\alpha_0}{2}\left(\frac{T-T_{c0}}{T_{c0}}\right)\overline{M}^2 - \frac{1}{6}\frac{H^2 N_R}{T}\overline{M}^2$$

$$- \frac{A}{4}\delta_R\overline{M} + \frac{1}{4}\beta\overline{M}^4. \qquad (16)$$

From (16) we immediately get the Curie temperature and the temperature dependence of the magnetization of a ferromagnet under illumination:

$$T_c = T_{c0} + \frac{T_{c0}}{\alpha_0}\left\{\frac{H^2 N_R}{3T_{c0}} + \frac{A}{2}\left[\frac{1}{2}n_R U + \frac{3}{4}AP\tau_r\frac{2m^*n_R}{(3\pi^2 n_R)^{\frac{2}{3}}}\right.\right.$$

$$\left.+ \frac{N_R H}{3T_{c0}}\frac{\tau_r}{\tau_u}\right]$$

$$\times\left(1 + P\tau_r + \frac{N_R}{n_R}\frac{\tau_r}{\tau_u}\right)^{-1}\right\}, \qquad (17)$$

$$\overline{M} = \left[\frac{\alpha_0}{\beta}\left(\frac{T_c-T}{T_{c0}}\right)\right]^{\frac{1}{2}} = S\left[\frac{5}{3}\left(\frac{T_c-T}{T_{c0}}\right)\right]^{\frac{1}{2}}. \qquad (18)$$

The first and second terms in the curly brackets in (17) describe the shifts of the Curie point due to defect-trapped and free photoelectrons, respectively.

Let us now find the anomalies in the behavior of the rate of entropy production $\dot{S}$ at the phase transition. This quantity, in neglect of radiative recombination of current carriers and with allowance for the fact that all the absorbed light energy is ultimately converted into heat, is given by the expression

$$\dot{S} = \omega n/T\tau_r. \qquad (19)$$

It has also been taken into account in (19) that in the steady state the rate of photon absorption is equal to the rate of recombination of free photoelectrons. It follows from (3)–(5) that at small magnetizations, when $A\overline{M} \ll \omega - E_g$, we can write

$$\dot{S}(\overline{M}) = \dot{S}(0)[1 - U^2\overline{M}^2/8], \qquad \dot{S}(0) = \omega n_R/T\tau_r. \qquad (20)$$

Analysis of relations (14), (17), (18), and (20) shows that at the phase transition point the rate of entropy production itself is continuous, but the derivatives of $\dot{S}$ with respect to temperature and with respect to the intensity and frequency of the light have finite discontinuities with values given by

$$\Delta\frac{\partial\dot{S}}{\partial T} = \frac{\dot{S}(0)U^2\alpha_0}{8T_{c0}\beta}, \qquad \Delta\frac{\partial\dot{S}}{\partial R} = -\frac{\dot{S}(0)U^2\alpha_0}{8T_{c0}\beta}\frac{\partial T_c}{\partial R}, \qquad (21)$$

$$\Delta\frac{\partial\dot{S}}{\partial\omega} = -\frac{\dot{S}(0)U^2\alpha_0}{8T_{c0}\beta}\frac{\partial T_c}{\partial\omega},$$

where the symbol Δ denotes the change in the quantity upon the transition of the system from the unmagnetized to the magnetized state. According to (19) and (14), the derivatives of the densities of free and trapped photoelectrons have similar anomalies.

Relations (14)–(17), (20), and (24) were obtained on the assumption that the densities of free photoelectrons, in the subbands do not reach the limiting values $n_{\omega\sigma}$ (6), i.e., that

$$n_R < n_\omega = [2m^*(\omega - E_g)]^{\frac{3}{2}}/3\pi^2. \qquad (22)$$

It is easy to obtain the corresponding formulas for the case in which the opposite inequality holds. Recognizing that in that case the free electron density is determined by (6) and that formulas (18) and (19) remain valid, we write the main results:

$$N = N_\omega = n_\omega(n_\omega/N_L + \tau_d/\tau_u)^{-1}, \qquad (23)$$

$$n_\uparrow - n_\downarrow = \delta_\omega = 3n_\omega U\overline{M}/2, \qquad (24)$$

$$T_c = T_{c0} + \frac{T_{c0}}{\alpha_0}\left\{\frac{H^2 N\omega}{3T_{c0}} + \frac{3}{4}An_\omega U\right\}, \qquad (25)$$

$$S(\bar{M}) = S(0)\,[1+3U^2\bar{M}^2/8], \quad S(0) = \omega n_u/T\tau_r, \quad (26)$$

$$\Delta\frac{\partial S}{\partial T} = -\frac{3}{8}\frac{S(0)U^2\alpha_0}{T_{c0}\beta}, \quad \Delta\frac{\partial S}{\partial R} = \frac{3}{8}\frac{S(0)U^2\alpha_0}{T_{c0}\beta}\frac{\partial T_c}{\partial R},$$

$$\Delta\frac{\partial S}{\partial\omega} = \frac{3}{8}\frac{S(0)U^2\alpha_0}{T_{c0}\beta}\frac{\partial T_c}{\partial\omega}. \quad (27)$$

Let us discuss these results for the Curie temperature of an illuminated ferromagnetic semiconductor. It follows from (17) and (25) that the relative change in T_c due to the localized photoelectrons is

$$t_l = H^2N/3T_{c0}\alpha_0 = (H/J_0S)^2Na^3. \quad (28)$$

Since H in (11) is proportional to J_0, this shift does not depend on the s-f exchange constant AS, unlike the shift due to the free electrons, which is described by the second terms in the curly brackets in (17) and (25) and is proportional to A^2S^2 [recall that for free electrons (17) and (25) hold only at the Fermi energy of the photoelectrons, which is higher than E_0 (2)]. Physically, result (28) is perfectly clear: the s-f exchange unites the spins of the atoms within a defect into a single cluster, but outside the defect this exchange can be manifested only implicitly, through the size of the cluster it creates.

Since $AS \gg T_{c0}$, in order for the shift of T_c due to electrons localized at defects to be comparable to the shift due to free photoelectrons, the density of the first must be several order of magnitude higher than that of the second. As we have mentioned above, such a situation is completely realistic.

According to (11), under the condition that the exchange radius r_0 is larger than the defect dimension r_d the quantity H/J_0S is equal to the number of lattice atoms on which the defect-trapped electron is localized . Even if this number is of the order of the number of nearest neighbors, at the typical parameter values $a = 5\cdot10^{-8}$ cm and $N = 10^{19}$ cm^{-3} the quantity t_l in (28) can reach 10%.

If the exchange interaction is only between nearest-neighbor spins,[1)] then for $r_d \gg a$ the quantity H/J_0S is proportional to the number of surface atoms of the defect. On the other hand, for a defect consisting of a central atom and its z nearest neighbors we have $H/J_0S = z-1$, and for a cubic lattice ($z=6$) we get $t_l = 25Na^3$. This estimate agrees in order of magnitude with the estimate obtained when T_c is evaluated using the density of long-wavelength magnon levels for $S=1/2$ in a crystal containing defects.[10]

5. LONG-LIVED COHERENT STATES

In this section we consider the situation which might exist[6] in EuCrO$_3$, viz., that illumination produces Frenkel excitons between which there can be an attractive force[11] giving rise to exciton complexes and, if the lifetime is sufficiently long, an excitonic phase having magnetic properties different from those of the unexcited crystal. The formation of the excitonic phase is accompanied by a decrease in the light absorption, since the frequency of the light should agree with the frequency of the exciton, and after one exciton is excited at an atom a second exciton can no longer be excited at it (optically induced transparency). Consequently, the

phase transition should occur with a decrease in the rate of entropy generation.

It is shown below that if the exciton band is sufficiently wide, the probability of radiationless multiphonon annihilation of excitons acutally falls off exponentially with increasing size of the excitonic-phase region. The Hamiltonian of a system consisting of Frenkel excitons and phonons is written as a sum of the free exciton Hamiltonian $\mathcal{H}_{ex}$, the free phonon Hamiltonian $\mathcal{H}_{ph}$, and the interaction Hamiltonians $\mathcal{H}_c$ and $\mathcal{H}_a$ between them, the first of which conserves the total number of excitons and the second of which does not:

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{ph} + \mathcal{H}_c + \mathcal{H}_a, \quad (29)$$

$$\mathcal{H}_{ex} = \nu\sum a_g^+a_g + \sum B(h)a_g^+a_{g+h}$$
$$-\frac{1}{2}\sum U(h)a_g^+a_ga_{g+h}^+a_{g+h},$$

$$\mathcal{H}_c = N_t^{-1/2}\sum A_{qs}\exp(iqg)Q_{qs}a_g^+a_g.$$

Here a_g^+ and a_g are the Pauli exciton operators, g is the number of the atom, the subscripts q and s of the normal coordinate Q_{qs} are the phonon quasimomentum and spectral branch, respectively, and N_t is the number of unit cells in the crystal. The Hamiltonian $\mathcal{H}_{ph}$ has the standard structure; the structure of $\mathcal{H}_a$ is unimportant.

The role of the zero-order Hamiltonian is played by $\mathcal{H}_0 = \mathcal{H} - \mathcal{H}_a$. In the adiabatic approximation its wave function is approximated by the expression (ω_{qs} is the phonon frequency and μ is the mass of the unit cell)

$$\psi = \Phi\prod_{qs}\chi_{qs}(Q_{qs}-\bar{Q}_{qs}),$$

$$(30)$$

$$\bar{Q}_{qs} = -A_{qs}\omega_{qs}^{-2}\mu^{-1}N_t^{-1/2}\sum_l\exp(iqg)(\Phi, a_g^+a_g\Phi).$$

Here Φ is the exciton wave function, and χ is a harmonic oscillator wave function. The probability of a transition from initial state i of Hamiltonian $\mathcal{H}$ to final state f is governed mainly by the exponential factor due to the change in the phonon equilibrium positions $\tilde{Q}_{qs}$ upon the transition[12-14]:

$$\omega_{if} \sim \exp[-(\varepsilon-E_p)/2\sigma^2],$$

$$E_p = \mu\sum_i\omega_{qs}^2|\delta\tilde{Q}_{qs}|^2, \quad \delta\tilde{Q}_{qs} = \tilde{Q}_{qs}^i - \tilde{Q}_{qs}^f, \quad (31)$$

$$\sigma^2 = \mu\hbar\sum\omega_{qs}^3|\delta\tilde{Q}_{qs}|^2(2n_{qs}+1),$$

where n_{qs} in the Bose distribution function for the phonons, and ε is the difference of the exciton energies between initial and final states. The structure of $\mathcal{H}_a$ affects only the pre-exponential factor in the expression for ω_{if}.

The sign of the exciton-exciton interaction in $\mathcal{H}_{ex}$ (29) corresponds to an attraction between excitons, which also gives rise to the excitonic phase. It is assumed that this phase in the initial state occupies a simply connected region $\mathcal{G}$ in which all L atoms are excited. In the final state one of the excitons within this region has vanished, i.e., an exciton hole

has appeared in it (the concept of a hole can be introduced not only for fermions but also for Pauli quasiparticles).

Depending on the relationship between the width W_h of the hole energy band, which according to (29) is proportional to B, and the maximum lattice-deformation energy E_p^m (31) of the hole, a hole can be can be either localized at a definite atom or spread out over the whole excitonic region. For $W_h \ll E_p^m$ the hole is localized at a definite atom (an anlog of a small-radius polaron). Then $\Phi_f(h) = a_h\Phi_i$, where Φ_i is the initial excitonic wave function and $\Phi_f(h)$ is the wave function on localization of the hole at atom h. Then, according to (30) and (31), neither $\delta\tilde{Q}_{qs}$ nor ω_{if} will depend on the size of the excitonic region.

A completely different situation occurs for $W_h \gg E_{ph}^m$, when the hole moves over the entire excitonic region and the coherence of this motion is manifested in the presence of a wave vector k:

$$\Phi_f(k) = \sum_{h\in\mathscr{G}} C_h(k) a_h\Phi_i. \qquad (32)$$

According to (30) and (32), the shift of the normal coordinate of the phonons is given by the expression

$$\delta\tilde{Q}_{qs}(k) \approx -\frac{A_{qs}}{\omega_{qs}^2\mu N_t^{1/2}}\frac{1}{L}\sum_{g\in\mathscr{G}}\exp(iqg). \qquad (33)$$

According to (31), exciton annihilation for $T \gg \omega_{qs}$ is an activational process. Since $\varepsilon \ll E_g$, the activation energy is $E_A \approx \varepsilon^2/4E_p$. For $T = 0$, exciton annihilation occurs as a result of the quantum tunneling of the lattice from the initial to the final equilibrium position of its atoms. Regardless of the temperature and the nature of the q dependence of ω_{qs} and A_{qs}, the annihilation probabiity (31) falls off with increasing L. This can be seen immediately from the fact that, according to (33), for $L \to \infty$ all the $\delta\tilde{Q}_{qs}$ with $q \neq 0$ go to zero. For long-wavelength acoustic phonons, ω_{qs} and A_{qs} are proportional to q. If this dependence is extrapolated to all q, the activation energy E_A comes out to be proportional to L, i.e., the annihilation probability falls off exponentially with increasing L. It falls off even more rapidly for $T \to 0$: the argument of the exponential in (31) is proportional not to L but to L^2. A similar situation obtains for optical phonons if ω_{qs} and A_{qs} are assumed to be independent of q.

Conditions are more favorable for exciton annihilation near the surface of the excitonic region. The energy of an exciton hole on the surface of the region is different from the energy in the interior, and this can give rise to a surface band. We shall assume that the corresponding states are concentrated in a surface layer having a thickness equal to the lattice constant. Taking $\mathscr{G}$ in (33) to mean a set $\mathscr{G}_S$ of surface atoms and L to be the number L_S of such atoms, we arrive at the conclusion that the activation energy in this case is proportional to L_S, i.e., to $L^{3/2}$.

A possible reason[6] for the absence of radiative annihilation of excitons is that the laser light does not directly excite long-lived excitons but some other high-frequency excitons, which are transformed through intermediate processes into low-frequency excitons for which radiative annihilation is forbidden.

The discussion given above refers to ideal crystals. Let us now consider how defects influence the excitonic phase. It is well known that in ordinary semiconductors the recombination of nonequilibrium current carriers takes place through defects, since they lift the restriction of momentum conservation. It is for this reason that the lifetime of these carriers in the excitonic droplets in Ge and Si does not depend on the size of the droplets. However, in the case under consideration here, the excitonic phase is made up of Frenkel excitons rather than Mott excitons. Therefore, the properties of this phase are different from those of the excitonic droplets mentioned above. First, the excitons here are excited at all the atoms within a certain region, and their concentration per atom of the semiconductor in the excitonic droplets remains small. Second, no metallization of the Frenkel excitons can occur here.

To clarify the physical picture, let us imagine that the excitons are at first excited at all the atoms of the crystal. Let us also assume that the crystal contains defects near which the exciton energy is lower than at a large distance from them. In the spectrum of the exciton holes such defects correspond to local levels lying above the energy band of these elementary excitations. Annihilation of the exciton through local levels is not limited by quasimomentum conservation, and the annihilation probability is therefore independent of the dimensions of the excitonic region.

Thus, after the light creating the excitons is turned off, the vanishing of the excitonic phase begins in the regions near defects, into which the excitons diffuse from other regions. But the diffusion of excitons is limited by the necessity of their escape from the excitonic phase, to which the excitons are bound by forces of attraction. Accordingly, the activation energy for the annihilation of excitons increases by an amount of the order of the energy of cohesion of the excitons in the excitonic phase. Since this energy does not depend on the size of the excitonic region, this exciton annihilation channel is the most effective. The physical situation is reminiscent of the evaporation of an evacuated liquid, and the process is also described by a diffusion equation with a moving boundary.

We note that a long lifetime of the excitonic phase can result not only from the specifics of the exciton-phonon interaction but also from some other effects. In any case, the above treatment demonstrates that it is possible in principle to have an excitonic phase with a long lifetime due to cooperative effects.

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[1] In this paper we have assumed that the radius of the exchange interaction is much larger than the lattice constant. However, this assumption was used only in the description of the free photoelectrons. Expression (28) is valid for an arbitrary exchange radius.

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Translated by Steve Torstveit