Optically induced magnetization and Mn spin-lattice relaxation in InP:Mn

R. Laiho, E. Lähderanta, E. Supponen, and L. Vlasenko*
Wihuri Physical Laboratory, University of Turku, SF-20500 Turku 50, Finland
(Received 31 October 1989)

Photomagnetization of InP doped with 8×10^{18} cm^{-3} Mn ions has been observed when pumping the sample with unpolarized light in an external magnetic field. The effect is attributed to enhancement of the spin polarization of localized magnetic moments by trapped photocarriers. Analysis of the temperature dependence of the photomagnetization signal shows that the spin-lattice relaxation of Mn^{2+} in InP is due to the one-phonon direct relaxation ($\sim T^{-1}$) for $T<8$ K and by the two-phonon Orbach-Blume relaxation ($\sim T^{-5}$) for $T>8$ K. Above 1 T, saturation of the photomagnetization is observed giving evidence for aligning of the spins in ferromagnetic spin clusters.

In recent years several investigations have been made into light-induced changes of the properties of dilute magnetic semiconductors. Ryabchenko, Semenov, and Terlistskii[1] have observed giant splitting of exciton luminescence lines in $Cd_{0.95}Mn_{0.05}Te$ when pumping the sample by light in an external magnetic field. The effect was attributed to exchange scattering of spins between localized magnetic moments and light-induced carriers which are not in spin equilibrium. By using a superconducting quantum interferometer (rf SQUID) Krenn *et al.*[2] have observed photomagnetization of $Hg_{1-x}Mn_xTe$ by pumping the sample with circularly polarized light. In this case the sample is magnetized by spin scattering between local moments and carriers oriented by transfer of angular momentum from light. Awschalom *et al.*[3] have used a sensitive dc-SQUID to investigate photomagnetization of $Cd_{0.8}Mn_{0.2}Te$. Applying the optical boxcar technique they were able to explore picosecond dynamics of magnetization including the formation of magnetic polarons.[4,5]

In this paper we will discuss optically induced magnetization of InP doped with 8×10^{18} cm^{-3} Mn ions. This is the first III-V compound semiconductor found to exhibit macroscopic magnetization under optical pumping. The obtained results provide information about the spin-lattice relaxation of the impurity ion in the sample.

In the experiments the sample is illuminated from the top of a dewar along a tube containing a lens system or an optical fiber. This tube ends with a section made out of fused silica and accommodates the sample holder, heater, and a thermometer. On its outer wall a detection coil is wound (10-mm diam) matched to the input of an rf-SQUID. The sample tube is fixed tightly on the axis of a superconducting solenoid, and the whole assembly is shielded against stray magnetic fields with superconducting and μ-metal shields. The sample is cooled by He exchange gas, and the temperature is measured with a carbon-glass thermometer. As the light source, a tungsten lamp is used followed by a filter. The photoinduced magnetization signal is detected with a lock-in amplifier connected to the output of the SQUID control electronics.

As discussed by Kaufman and Schneider,[6] the charge state of Mn in InP is a matter of controversy. Results of electron-spin-resonance (ESR) measurements[7] and those of optically detected magnetic resonance[8] and Hall-effect measurements[9] have been explained by models involving the Mn^{2+} charge state from the $3d^5$ configuration and a hole bound loosely to the impurity ion. The alternative possibility is Mn^{3+} with the $3d^4$ electron configuration.[10] Agreeing with our earlier data for InP:Mn (Ref. 11), the magnetic susceptibility of the sample, as shown in Fig. 1, obeys the Curie-Weiss law. However, the plot of $1/\chi$ reveals a small positive value of the Curie temperature, $\theta=0.5$ K, as determined by fitting the data to the equation $\chi(T)=\chi_d+N\mu_B^2p_0^2[3k_B(T-\theta)]^{-1}$, where χ_d is the diamagnetic contribution (-3.3×10^{-3} J T^{-2} kg^{-1}) and $p_0=g[S(S+1)]^{1/2}$ the effective Bohr magneton number. The value of $g=2.0$ was obtained from ESR measurements. The magnetization of the sample was found to obey the formula $M(H,T)=Ng\mu_BSB_S(Sg\mu_BH/k_BT)$, where B_S is the Brillouin function with $S=\frac{5}{2}$ and $N=8\times10^{18}$ cm^{-3}.

The positive value of θ is indicative of ferromagnetic interactions in the sample. All alloy systems possess some degree of atomic short-range order. As shown by Morgonwick and Mydosh[12] for AuMn and CuMn it is this spatial distribution of the magnetic impurities in the nonmagnetic hosts which determines the type of magnetic interactions. They used a cluster model containing singlets, pairs, and triplets of the magnetic atoms. Essentially the same method, extended nearest-neighbor-pair (ENNP) approximation (Ref. 13) has been successfully used for description of magnetic properties of Mn-based semimagnetic semiconductors.[14] In semiconductors containing magnetic impurities there is a large exchange interaction between carrier spins and the spins of the magnetic ions surrounding the carrier. The energy of conduction electrons is at minimum if ordering is of ferromagnetic type.[15] Therefore, there is a tendency for self-trapping and impurity localization of carriers in ferromagnetic regions.

An example of light-induced magnetization signal, M_{opt}, when pumping the InP:Mn sample by unpolarized

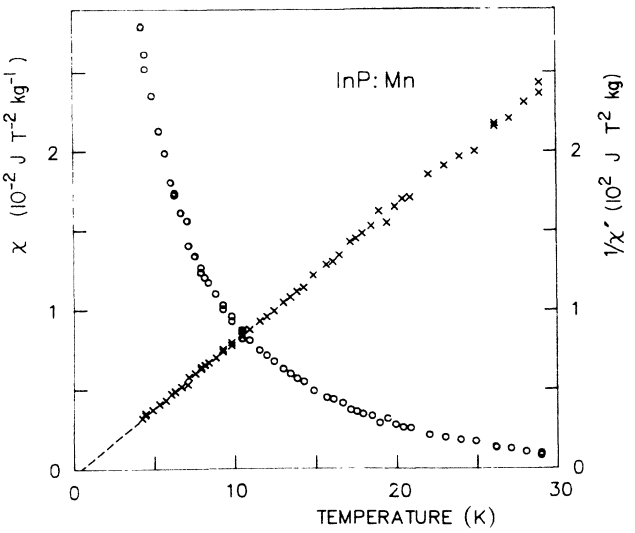

FIG. 1. Temperature dependence of the magnetic susceptibility of InP containing 8×10^{18} cm^{-3} Mn ions.

light is shown in Fig. 2. The absolute value of M_{opt} was determined by calibrating the magnetometer with a coil having the same diameter as the sample, 3 mm. For phase-sensitive detection the pumping light was chopped at the frequency of 67 Hz. The level of the noise in the measurements was about $2\times10^{-4}\Phi_0$, where Φ_0 is the magnetic-flux quantum (2.07×10^{-15} Wb). Using different optical band filters, the pumping was made at wavelengths in the region of the band edge ($E_g=1.42$ eV) or deeper in the conduction band. No dependence of M_{opt} on pumping wavelength was observed in this way.

The plot of M_{opt} versus pumping power density was found to be approximately linear in the range of small pumping powers. A complete saturation was observed when increasing the light intensity. This behavior is similar to that of photoconductivity of semiconductors at low temperatures and probably results from the presence of carrier trapping centers in the sample (see Ref. 16, p. 325). All the subsequent measurements were made at power densities in the linear part of the plot of M_{opt} in Fig. 2.

When photoexcited carriers are generated, they possess high kinetic energy. After thermalization near to the lattice temperature they may become captured by trapping centers. As already mentioned, one way to localize the carrier spin is trapping near the band edge in a region where the effective magnetic field is large due to the presence of magnetic impurities or their complexes.[15] In semimagnetic semiconductors the strong spin-exchange interaction between the holes bound at acceptor sites (or electrons bound to donors) leads to formation of bound magnetic polarons (BMP).[5] Considering the acceptor properties of Mn^{2+} in InP and its tendency to bind holes,[8] we emphasize the similarity between the suggested trapping of spins in our sample and the BMP problem in semimagnetic semiconductors.

As is shown in Fig. 3 the low temperature part of M_{opt} is proportional to T^{-1}. This suggests that the relaxation of the Mn spins is attributable to the one-phonon direct relaxation.[17] For $T>8$ K the experimental points can be well fitted with T^{-5}. This behavior is consistent with the spin-lattice relaxation observed for Mn^{2+} in BaF_2 and SrF_2 (Ref. 18) as well as in InP between 40–200 K.[7] The T^{-5} dependence can be connected to the Orbach-Blume relaxation[19] which is a two-phonon process with the participation of multiplet states lying close to one another.

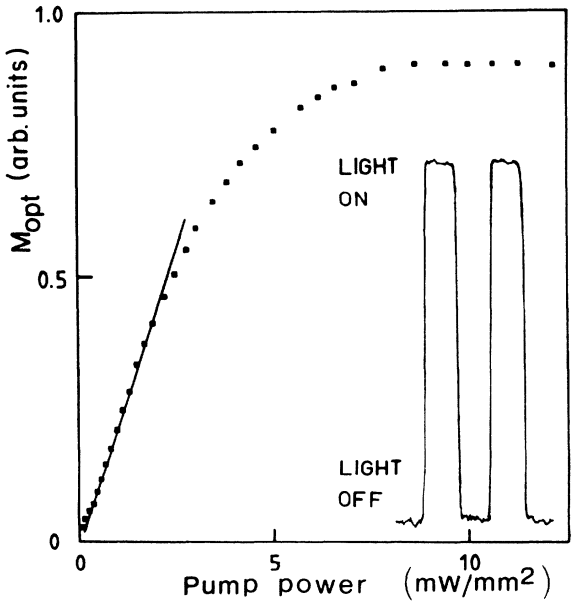

FIG. 2. Dependence of the light-induced magnetic moment on optical pumping power. In the right-hand corner of the figure is shown a typical signal appearing at the output of the lock-in amplifier.

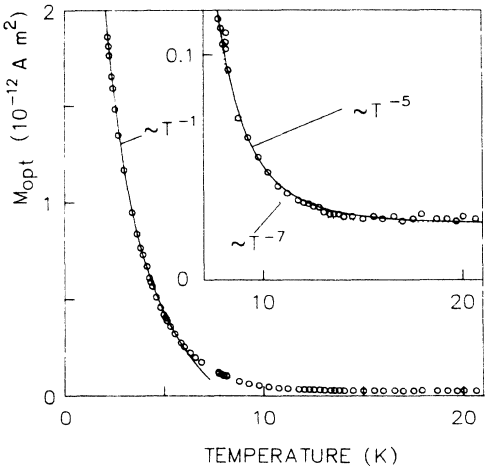

FIG. 3. Temperature dependence of the light-induced magnetic moment (open circles). In the inset is shown the high temperature part of the data in an expanded scale. The solid lines represent for the best fits of the experimental results to functions of the form $\sim T^{-1}$ and $\sim T^{-5}$. The T^{-7} dependence is shown for comparison (dotted line). The value of the external magnetic field is 5 mT.

Along with the suggestion[10] that the oxidation state of Mn in InP would be Mn^{3+}, the ground state of the ion would be split by the Jahn-Teller effect to a singlet ^5B and to a doublet ^5E located at an energy of $3E_{JT}$ above the singlet. With a conceivable Jahn-Teller energy $E_{JT} \simeq 480$ cm^{-1} (Ref. 10) the ^5E state would lie above the allowed phonon spectra of the crystal with the consequence that the spin-lattice relaxation would take place via the second-order Raman process with a predicted dominance of a T^{-7} term over T^{-5}.[19] As shown in the inset of Fig. 3 our results for $T > 8$ K can be fitted better with the T^{-5} than with the T^{-7} dependence. Although the difference of the two plots is not very large, it gives support to the interpretation that the oxidation state of Mn in InP is Mn^{2+} rather than Mn^{3+}.

Formation of ferromagnetic spin clusters in EuTe has been explained by an overlap of wave functions of impurity electrons with neighboring Eu ions.[20] Spins of the magnetic ions in the cluster are ferromagnetically coupled giving a large magnetic moment parallel to the spin of the electron. Assuming that in InP:Mn the exchange interaction between the Mn moments and spins of trapped photocarries is responsible for the observed photomagnetization, we find that the relaxation of the coupled system still occurs through the Mn-ion spin-lattice relaxation. This is consistent with long lifetimes of trapped carriers, tens of milliseconds for shallow traps as evidenced by photoconductivity measurements.[16] For rare-earth paramagnetic ions the spin-relaxation times are of the order of 10^{-3} s and somewhat shorter for the iron group.[17]

Denoting the spin-up and spin-down Mn ions as N_+ and N_-, we write the rate equation governing the magnetization $M_{opt} \sim g\mu_B(N_+ - N_-)\langle S_z \rangle$ as

$$\frac{\partial(N_+ - N_-)}{\partial t} = \frac{n_+^e - n_-^e}{T_{eM}} + \frac{n_+^h - n_-^h}{T_{hM}} - \frac{N_+ - N_-}{T_{Ml}} , \tag{1}$$

where T_{iM} $(i = e,h)$ and T_{Ml} are the electron-Mn, hole-Mn and Mn-lattice spin-relaxation times, respectively. The rate equations for the photocarriers can be written as

$$\frac{\partial(n_+^i - n_-^i)}{\partial t} = g_+^i - g_-^i - \frac{n_+^i - n_-^i}{\tau} - \frac{n_+^i - n_-^i}{T_{il}} - \frac{n_+^i - n_-^i}{T_{iM}} , \tag{2}$$

where g_+^i and g_-^i are the generation rates of spin-polarized carriers, τ is the lifetime of carriers trapped at a localized magnetic moment, and T_{il} the carrier spin-phonon relaxation time. In the stationary state M_{opt} is proportional to

$$N_+ - N_- = T_{Ml}\left[\frac{g_+ - g_-}{T_{eM}(\tau^{-1} + T_{el}^{-1} + T_{eM}^{-1})} + \frac{g_+^h - g_-^h}{T_{hM}(\tau^{-1} + T_{hl}^{-1} + T_{hM}^{-1})}\right] . \tag{3}$$

If the number of e-h pairs created in a unit time is n_0, then $g_+^i - g_-^i \propto n_0\tau^*/T_{Mi}$ where τ^* is the lifetime of a free carrier, and T_{Mi} is the Mn-carrier spin-polarization time. With $\tau^* \simeq T_{el} \simeq 10^{-9}$ s, $T_{hl} \simeq 10^{-12}$ s [as in another A_3B_5 semiconductor GaAs (Refs. 21 and 22)], $T_{el} \gg T_{eM} \simeq T_{hM} \simeq 10^{-12}$ s (Refs. 1 and 2), and τ^* the same for electrons and holes, Eq. (3) is reduced to

$$N_+ - N_- \propto n_0\tau^* T_{Ml}\left[T_{Me}^{-1} + \frac{T_{Mh}^{-1}}{2}\right] . \tag{4}$$

From comparison with the temperature dependence of the relaxation times observed in GaAs (Refs. 21–23) it can be suggested that in the conditions of the present experiment ($T < 15$ K), the only temperature-dependent relaxation time in (4) is T_{Ml}.

Magnetic field dependence of the photomagnetization signal is shown in Fig. 4 together with the magnetization predicted by the Brillouin function $B_{5/2}(\frac{5}{2}\mu_B H/k_B T)$. It is found that M_{opt} obeys the field dependence of $B_{5/2}$ up to $H \simeq 0.8$ T, but then starts to saturate when H is increased. This saturation is interpreted as aligning of the spins in the ferromagnetic spin clusters. In our experiments the thermal average of the Mn spin component is $\langle S \rangle = SB_S(S\mu_B H/kT) \simeq 3\times10^{-3}$ in a typical measuring field of $H = 5$ mT and $T = 2$ K. From the value of $M_{opt} = 2\times10^{-12}$ A m^2 we estimate that the number of spin-polarized ions in the sample at 2 K was $N_+ - N_- \simeq 4\times10^{13}$. The measurement was made with an excitation power of 6 mW through a filter with the center frequency at 1.5 eV. Supposing that the efficiency of producing e-h pairs by light is 40%, the number of induced photocarriers in the sample is 2×10^{16} s^{-1}. The contributions from electrons and holes is expected to be additive.[1] If 0.5% of carriers becomes trapped near the magnetic ion sites, one obtains from (4) with the given relaxation times the value of $T_{Ml} \simeq 6\times10^{-4}$ s. This is a reasonable result, but it must be noted that large uncer-

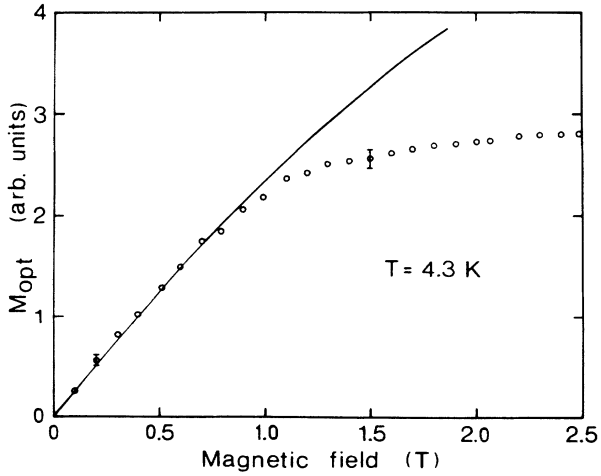

FIG. 4. Magnetic field dependence of the photoinduced magnetization signal. The solid line shows the Brillouin function for $S = \frac{5}{2}$ and $g = 2$.

tainties are involved in the parameters needed in the calculation.

The level of Mn impurities in our sample, 8×10^{18} cm^{-3}, is much below the concentration of magnetic ions in typical semimagnetic semiconductors. Considering the relatively good signal to noise ratio in the experiment and the possibility to use higher magnetic fields, we should be able to detect light-induced magnetization at impurity concentrations of about 10^{16} cm^{-3}.

To summarize, we have observed magnetization induced by unpolarized light in InP doped with manganese. The effect is attributed to trapping of photoexcited carriers near to magnetic impurities to form clusters of spins polarized by the carrier-Mn exchange interaction. With the used method it is possible to investigate the temperature dependence of the spin-lattice relaxation process of magnetic impurities at concentrations where the application of conventional methods such as ESR is limited by mutual magnetic interactions. In fields above 1 T saturation of the photomagnetization signal is observed giving evidence for the aligning of the spins in ferromagnetic spin clusters. It is expected that the effect discussed here is observable in a number of other III-V compound semiconductors doped with different magnetic impurities. Some of these materials, like InP:Fe are of interest for applications as radiation detectors or substrates for microwave devices.

The authors are indebted to Professor B.P. Zacharchnya for his interest and discussions.

---

*Permanent address: A.F. Ioffe Physico-Technical Institute of the Academy of Sciences of the U.S.S.R., 194 021 Leningrad, U.S.S.R.

[1]S. M. Ryabchenko, Yu G. Semenov, and V. V. Terletskii, Zh. Eksp. Teor. Fiz. **82**, 951 (1982) [Sov. Phys.—JETP **55**, 557 (1982)].

[2]H. Krenn, W. Zawadzki, and G. Bauer, Phys. Rev. Lett. **55**, 1510 (1985).

[3]D. D. Awschalom, J. Warnock, J. R. Rozen, and M. B. Ketchen, J. Appl. Phys. **61**, 3532 (1987); D. D. Awschalom, J.-M. Halbout, S. von Molnar, T. Siegrist, and F. Holtzberg, Phys. Rev. Lett. **55**, 1128 (1985).

[4]M. Nawrocki, R. Planel, G. Fishman, and R. Galazka, Phys. Rev. Lett. **46**, 735 (1981).

[5]D. Heiman, Y. Shapira, and S. Foner, Solid State Commun. **45**, 899 (1983).

[6]U. Kaufman and J. Schneider, Adv. Electron. Electron Phys. **58**, 81 (1982).

[7]M. N. Barbaschev, V. P. Maslov, and V. F. Masterov, Fiz. Tverd. Tela **25**, 1130 (1983) [Sov. Phys.—Solid State **25**, 648 (1983)].

[8]Y. Dawei, B. C. Cavenett, and S. M. Skolnick, J. Phys. C **16**, L647 (1986).

[9]E. V. Vavilov, L. F. Zakharenkov, and S. M. Mikhrin, Fiz. Tekh. Poluprovodn. **21**, 813 (1987) [Sov. Phys.—Semicond. **21**, 813 (1987).

[10]D. G. Andrianov, A. S. Savel'ev, and S. M. Yakubenya, Fiz. Tekh. Poluprovodn. **20**, 1235 (1986) [Sov. Phys.—Semicond. **20**, 791 (1986)].

[11]R. Laiho, J. Vanhatalo, and L. Vlasenko, *Proceedings of the International Conference on Magnetism* [J. Phys. (Paris) Colloq. (Suppl. 12) **49**, C8-871 (1988)].

[12]A. F. J. Morgonwick and J. A. Mydosh, Solid State Commun. **47**, 321 (1983).

[13]K. Matho, J. Low Temp. Phys. **35**, 165 (1979).

[14]J. C. van Gool and W. J. M. de Jonge, Phys. Rev. B **33**, 7637 (1986); A. Twardowski, H. J. M. Swagten, W. J. M. de Jonge, and M. Demianiuk, *ibid.* **36**, 7013 (1987).

[15]E. L. Nagaev, Phys. Status Solidi B **145**, 11 (1988).

[16]R. H. Bube, *Photoconductivity of Solids* (Wiley, New York, 1960), pp. 283 and 325.

[17]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), p. 557.

[18]J. B. Horak and A. W. Nolle, Phys. Rev. **153**, 372 (1967).

[19]R. Orbach and M. Blume, Phys. Rev. Lett. **8**, 478 (1962).

[20]J. Vitins and P. Wachter, Solid State Commun. **13**, 1273 (1973).

[21]A. H. Clark, R. D. Burnham, D. J. Chadi, and R. M. White, Solid State Commun. **20**, 385 (1976).

[22]G. E. Pikus and A. N. Titkov, in *Modern Problems in Condensed Matter Sciences,* edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1984), Vol. 8, p. 73.

[23]Wolfgang Kauschke, Narcís Mestres, and Manuel Cardona, Phys. Rev. B **35**, 3843 (1987).