PHYSICS OF MAGNETIC SEMICONDUCTORS

E.L.NAGAEV

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Laser Physics

L. TARASOV, Cand. Sc. (Phys.-Math.)

This book aims at bringing the reader up-to-date with the latest achievements and trends in the physics of laser processes, as well as at providing sufficient information so that the reader can then independently make use of the specialized literature in this field. It describes the present state of affairs in the development of laser technology from the point of view of research as well as applications in various branches of industry.

The three main aspects considered in this book are: methods for obtaining inverted active media, generation of radiation field in a resonator, and the dynamics of laser processes. A systematic description has been given of the methods, approaches and approximations used in the laser theory. Intended for scientists and engineers engaged in laser research, this book can also be quite useful for students and teachers in universities.

An Introduction to Statistical Physics

A. VASILYEV, D. Sc. (Phys.-Math.)

Based on lectures read by the author to students of the department of engineering electronics at the Moscow Power Engineering Institute for a number of years, the present book treats statistical physics with an accent placed on its application to fields associated with electronics. In these and similar fields, acquaintance with the fundamentals of statistical physics of non-equilibrium states (kinetics) is very important because a foundation is set up helping to master special subjects dealing in some way or other with the flow of an electric current in gases, semiconductors, and metals.

In acquainting the reader with the basic methods and concepts of statistical physics, the author illustrates all the material with examples, following the well justified principle: from concrete to abstract, from simple to complicated material.

The book is intended for students of higher educational institutions who have completed a course in mathematics and general physics.

A Survey of Semiconductor Radiation Techniques

Edited by L. SMIRNOV, D. Sc. (Phys.-Math.)

This book has been written for two sorts of people primarily The first group includes the engineers, technicians, and research workers who are entering upon active work of exploration of new areas of semiconductor technology. The second type of person for whom the book is intended is the college student or post-graduate who may use the book as a source of general information about the subject.

The book supplies a specific information on radiation defects in semiconductors and discusses, with reliance on particular examples, the feasibility of employment of said defects for technological purposes. Ample space is given in this book to treatment of the problems relating to radiation control. Point defects, disordered regions, disordered and amorphous layers obtained as a result of irradiation of semiconductor materials, the properties and stability of such defects, doping by ion implantation and nuclear transmutation, ionic and radiation-enhanced diffusion are the topics taken up by this book.


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PHYSICS OF MAGNETIC SEMICONDUCTORS

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CONTENTS

This introduction aims to provide a general presentation of the electrical, optical and magnetic properties of those transition-metal or rare-earth compounds that are known as magnetic semiconductors (MS)*. It should be made clear at once, however, that the term "magnetic semiconductor" is only accurate for the electric properties of those materials that are always greatly affected by a magnetic order. As far as the magnetic properties are concerned, conduction electrons influence them noticeably only when the electron density becomes large enough and so the same materials (e.g. EuO, EuS), considered from the point of view of their magnetic properties, are often classified as magnetic insulators. On the other hand, some highly imperfect crystals that are actually degenerate semiconductors are numbered among the magnetic metals (e.g. GdN, HoN). In the wider sense of this term, MS also include the ferrites, but these are not specially discussed in this book, although several theoretical results contained herein are also applicable to ferrites. Detailed information about the properties of ferrites may be found in [389].

Magnetic semiconductors possess a number of unique properties. For instance, their magnetoresistivity and spontaneous Faraday rotation of the polarization plane of light are by several orders of magnitude greater than those of magnetic metals. Some of their properties are even unparalleled in other materials, for example, a giant red shift of the optical absorption edge and photoconductivity threshold when magnetic semiconductors are magnetized.

It was for magnetic semiconductors that the novel physical phenomenon of heterophase autolocalization of conduction electrons** was first predicted and experimentally detected. The essence of this phe-

* The following abbreviations are used throughout: FM for ferromagnetic, FIM for ferrimagnetic, AF for antiferromagnetic, CAF for canted antiferromagnetic, and PM for paramagnetic; MS, FMS and AFS for magnetic, ferromagnetic and antiferromagnetic semiconductors, respectively.

** The concept of the heterophase autolocalization of electrons was first formulated and argued in papers [194, 195] by the author of this book. Papers by N. Mott [278], M.A. Krivoglaz [426], T. Kasuya [204-208] containing similar results appeared considerably later. The author was also the first to prove the possibility of a collective heterophase autolocalization in degenerate semiconductors [197, 46].

nomenon in nondegenerate semiconductors is that a conduction electron creates in the crystal a region of a phase that is normally unstable but then stabilizes the phase by being localized within the region. The result is the production of a new type of quasi-particle. For instance, in a nondegenerate antiferromagnetic semiconductor the electron may become self-trapped inside a ferromagnetic microregion.

In degenerate semiconductors a collective heterophase autolocalization of charge carriers is also possible. The result is a new type of state where a homogeneous crystal splits up into alternating regions of normally stable and normally unstable phases with all the electrons assembling in the latter. For instance, an AF crystal splits up into FM and AF regions with all the electrons concentrating in the FM phase. Such a state could be interpreted as a superposition of very high-amplitude charge-density and spin-density waves. In principle, the structures that result from the superposition of relatively low-amplitude charge-density and spin-density waves are also possible in degenerate semiconductors, such structures being similar to the "incommensurate" structures that are observed earlier in low-dimensional nonmagnetic materials.

MAGNETIC AND SEMICONDUCTING PROPERTIES

All sorts of magnetic orderings are possible in MS. Antiferromagnetic semiconductors have been known long ago, and there is a large number of them. However, not a single ferromagnetic semiconductor had been discovered until 1960; indeed, an opinion had been voiced that ferromagnetic and semiconducting properties were incompatible. However, after Tsubokawa [10] succeeded in producing the first FMS, $CrBr_3$, thus proving their existence, other FMS soon followed and at present their number is close to 100. Of the magnetic semiconductors the chalcogenides of europium (the FMS's: EuO, EuS and the AFS's: EuTe, EuSe) as well as the chrome chalcogenide spinels (the FMS's: $CdCr_2Se_4$, $HgCr_2Se_4$ etc.) attracted the most attention from scientists.

The electrical properties of low-doped AFS are qualitatively similar to those of nonmagnetic semiconductors: their conductivity grows exponentially with the temperature. A long-standing assumption has been that it is small polarons which act as the charge carriers in many of them, e.g. in NiO. These move across the crystal by hopping from one atom to another, the directions of successive hops being uncorrelated. This is the radical difference between the hopping and band mechanisms of motion. The mobility of small polarons, in contrast to that of electrons, grows exponentially with the temperature. However, a necessary condition for the existence of small polarons is that the width of the conduction or the valence band be

small compared to the lattice polarization energy by an electron at rest. This is a very stringent condition, and, as is shown by analysis, is not fulfilled in any of the magnetic semiconductors known at pre sent. If this condition is not fulfilled, a polaron existing in the crystal must be a large one for which the quasi-momentum is a well-defined quantum number, and the only difference between it and the usual band electron, from the viewpoint of its mechanism of motion, would be a somewhat larger effective mass. For this reason polaron effects would not bring about a qualitative change in the electric properties of magnetic semiconductors compared with nonmagnetic ones.

However, a sharp difference between the properties of FMS and of nonmagnetic semiconductors becomes apparent immediately. It manifests itself first and foremost in the so-called giant red shift of the optical absorption edge, which takes place as the temperature is lowered starting already in the paramagnetic region [85]. The decrease in the width of the optical gap with decreasing temperature amounts to 0.5 eV for some FMS's. In nonmagnetic semiconductors the shift is a blue one and is several orders of magnitude smaller. At a fixed temperature, the red shift can be induced by an external magnetic field, this being the case not only with FMS's, but with AFS's as well. This is unambiguous proof that the red shift is caused by the magnetization of the crystal.

On the other hand, the resistivity of nondegenerate FMS's frequently does not decrease monotonically with the temperature, as is the case with nonmagnetic semiconductors, but displays a sharp peak in the region of the Curie point T_c. Its relative height depends on the density of defects and may be several orders of magnitude high. The resistivity drops with increasing magnetic field, an especially drastic reduction occurring in the magnitude of the resistivity peak. The magnetoresistance in this region exceeds that of nonmagnetic semiconductors by several orders of magnitude, an additional difference being that in case of magnetic semiconductors the magnetic field does not raise, but on the contrary, reduces the magnetoresistance. These results are clear proof of a strong interaction between the charge carriers and the subsystem of magnetically ordered spins in MS.

MAGNETIC SEMICONDUCTOR MODEL AND SPINPOLARONS

Most of the principal properties of MS are in the majority of cases satisfactorily described by the *s-d* (or *s-f*) Vonsovsky model. This model, which for the sake of generality is referred to below as the *c-l* model, presumes that the crystal contains magnetic ions with nonzero spins of *d*- or of *f*-shells ("*l*-spins"). An exchange interaction occurs between the localized *l*-spins of these ions which establishes a magnet-

ic ordering of some type in the crystal, and, in the majority of cases, these interactions may be described by the Heisenberg Hamiltonian.

In addition to the localized electrons of partially-filled shells, the crystal also contains delocalized conduction electrons ("c-electrons") and holes. In the simplest case these electrons occupy states in an s-type band and c-l exchange interaction takes place between the c-electrons and the l-spins. It is this interaction that is responsible for the dependence of the charge carrier states on the ordering of the l-spins.

Such a model is, for example, directly applicable to the chalcogenides of Eu where the c-band states are constructed from the $6s$- and $5d$-type states, but the l-spins are f-type. However, in some materials the c-band states may be constructed from the same atomic states as the l-states. For example, in the FMS $CdCr_2Se_4$ the Cr ions are normally in the Cr^{3+} state. The appearance of a conduction electron in the crystal means that one on the ions becomes Cr^{2+}. In an ideal crystal, all the Cr ions are equivalent, and so each Cr ion must have the same probability to be in the Cr^{2+} state. In this case the motion of a c-electron in the crystal takes place as a result of the recharge reaction $Cr^{2+} + Cr^{3+} \rightarrow Cr^{3+} + Cr^{2+}$.

In terms of the c-l model, this situation corresponds to such a strong c-l exchange that the conduction-electron spin combines with the spin of the ion, to which at that moment it belongs, to form a single spin. For an ionic l-spin equal to S, the total spin is equal to $S + 1/2$ or $S - 1/2$, depending on whether the c-l exchange integral A is positive or negative. Following the transition of the c-electron to another atom, the spin of the c-electron combines with the l-spin of the new atom to form a single spin [69]. Hence, the motion of a charge carrier in the crystal is equivalent to the motion of an "irregular" spin $S \pm 1/2$. In contrast to a conventional band electron, this quasi-particle, termed a spinpolaron in [70]*, cannot be assigned a definite spin projection. The precondition for its existence is that width W of the c-band is small compared to the c-l exchange energy AS. However, spinpolaron effects can also appear in the opposite limit $W \gg AS$.

It should be emphasized that combining the c-electron spin with the l-spin into a single spin does not mean that the spinpolaron wanders about the crystal in random walks. For instance, in an FMS at $T \ll T_c$ one may introduce the concept of a quasi-momentum for the spinpolaron, i.e. it moves in accordance with the band mecha-

* To avoid misunderstanding, it should be noted that some authors apply the term "spinpolaron" to quite different states. In [69], where the two-atom problem is treated, the term "double exchange" is used but this is inadequate for many-atom systems.

nism. At $T \gtrsim T_c$ it is no longer possible to introduce a quasi-momentum for the spinpolaron, however, in this case its mobility is not temperature-activated.

RED SHIFT AND CONDUCTION ELECTRONS IN THE VICINITY OF THE CURIE POINT

Within the framework of the *c-l* model it is possible to provide a satisfactory explanation for the red shift of the absorption edge in an FMS. Should the *c-l* exchange interaction be considered using the perturbation theory, the shift in the energy of an electron having a spin projection σ would be equal in the first order in AS/W, to $(-A\sigma\mathfrak{M})$, where $\mathfrak{M}$ is the crystal magnetic moment per atom. Hence, if the electron spin projection is such that $A\sigma$ is positive, the electron energy will decrease as the magnetization is increased. This is equivalent to a reduction in the width of the gap in the energy spectrum.

Thus result is only a crudely qualitative. A more detailed consideration proves that the electron energy is nonanalytic in the *c-l* exchange, i.e. that the energy cannot be expanded in powers of AS/W. This means that generally it is impossible to apply the perturbation theory in AS/W. The physical explanation for this is that the electron energy is not in fact determined by the long-range, but by the short-range magnetic order. To be persuaded of this, consider the well-known expression for the electron energy in a crystal with a helicoidal magnetic ordering (3.2.6), the energy being accurately determinable at $T = 0$ in the limit of classically large spins S. The expression reveals that the *c-l* exchange shift in the energy of an electron at the bottom of the conduction band, in case of a large period of the helicoidal structure, practically coincides with the appropriate quantity in a ferromagnet, which is equal to $(-|A|S/2)$. At the same time, whereas the average of the crystal moment per atom $\mathfrak{M}$ in the ferromagnetic state is indeed S, for the helicoid $\mathfrak{M} = 0$. The physical explanation is based on the fact that, because of a slow variation of the direction of the local moment in space, the spin of the conduction electron has ample time to arrange itself in accordance with the local moment and will always point in its direction, as is the case of a ferromagnet. In fact, this is a sort of a spinpolaron state.

The inapplicability of the perturbation theory for the *c-l* exchange manifests itself especially strongly in the vicinity of the Curie point T_c where the direction of the local moment also varies slowly in space, although there is, in contrast to the helicoid, no periodicity in the directions of the spins. Calculations in [93] demonstrate that the *c-l* shift remains rather large at the Curie point being of the order of $|AS|^{4/3} W^{-1/3}$, i.e. much larger than A^2S^2/W one would obtain from the perturbation theory. This result explains why a sub-

stantial red shift of the absorption edge takes place with falling temperature even before the Curie point is reached.

The red shift of the absorption edge is also obtained for spinpolarons appearing in the limit of very strong c-l coupling $W \gg AS$. In this case the red shift is not determined by the c-l exchange integral A, but by the width of the conduction band W, i.e. it retains a reasonable value even as $AS \to \infty$. The temperature dependence of the spinpolaron spectrum makes itself manifest by the narrowing of its energy band with growing temperature.

One interesting and, as yet, unresolved problem in FMS physics is whether the c-electrons experience maximum scattering by spin fluctuations in the vicinity of T_c. Neutrons are well known to display such a maximum, but the electrons in perfect specimens of FM metals do not. The situation in an FMS is much more complicated than in metals, since not only is the mobility of the c-electrons temperature-dependent in the FMS, but so too is their density. The latter in impurity semiconductors often has a minimum in the vicinity of T_c and in this background it would not have been easy to discover a mobility minimum, even if one had been present. At the same time it has not been possible to study an FMS with intrinsic conductivity in the region of T_c.

As yet, it has not been possible to arrive at definite conclusions about the existence of a maximum in the scattering of c-electrons by critical fluctuations of the magnetization purely from theoretical considerations. By now numerous papers have accumulated in which the mobility is calculated in the Born approximation in the c-l exchange, with various approximations being used for the spin correlation functions. But the authors fail to take into account that this approximation is inapplicable in the vicinity of T_c (see Sec. 4.4) and for this reason the respective results may not be regarded as reliable. On the other hand, a procedure, which takes account of the realignment of the c-electron spins parallel to the local moment and which thus goes beyond the limits set by the Born approximation, enables only an estimate of the relaxation time in the vicinity of T_c to be obtained. Still, this estimate shows the mobility minimum in the vicinity of T_c is either shallow or completely nonexistent. This result agrees with the experimental data on the photoconductivity of perfect FMS crystals: its minimum in the region of T_c is either nonexistent or very shallow.

INDIRECT EXCHANGE VIA CONDUCTION ELECTRONS IN MAGNETIC SEMICONDUCTORS

As has already been discussed in the previous section, the appearance of the FM ordering shifts the bottom of the conduction band downwards and because the establishment of an FM ordering reduces the