

Doped EuTe: A mixed magnetic system

J. Vitins and P. Wachter

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, 8049 Zürich, Hönggerberg, Switzerland

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The additional magnetic exchange introduced by doping of the magnetically ordering Eu chalcogenides has been investigated in the case of antiferromagnetic EuTe by means of the Faraday rotation, optical absorption, reflectivity measurements, luminescence, and photoconductivity. The magnetic contributions due to the electrons which were introduced by doping could always be well distinguished by comparison with measurements on undoped samples. Our results lead to the conclusion that at least in the nondegenerate EuTe the introduced electrons form large spin dressed particles, namely magnetic polarons or at low temperatures ferromagnetic spin clusters which can extend over as many as 2000 Eu ions. The size of these clusters and their degree of magnetic order is, however, dependent on temperature, applied magnetic field, and on the concentration of dopant. The existence of these spin clusters was verified by the observation of domain patterns with a polarizing microscope. Novel also is our discovery of a very large wavelength-independent Faraday rotation, which reaches values of up to 3600 deg/cm at 4.2 K. We have attributed this Faraday rotation to magnetic resonance of the spin clusters in the exchange fields of the magnetic sublattices.

I. INTRODUCTION

The Eu chalcogenides have in the past decade attracted much interest, predominantly because of the unique physical properties which arise from the strongly localized $4f$ electrons of the Eu ions. The position in energy of the $4f$ electrons is between well-separated valence and conduction bands and they yield a spin-only magnetic moment of $7\mu_B$. The magnetic behavior of these semiconducting or insulating materials has been described by means of an ideal Heisenberg model.¹ The magnetic order of the Eu spins in the *pure* crystals is determined by the competitive interactions of an antiferromagnetic superexchange via the anion lattice and a ferromagnetic indirect exchange through overlapping Eu $5d$ (t_{2g}) orbitals.² It has been shown that, at least in the case of EuO, these orbitals constitute the lowest conduction band.³ The ferromagnetic exchange J_1 is strongly dependent on the lattice constant and it is larger than the antiferromagnetic coupling $|J_2|$ in EuO and EuS, which therefore order ferromagnetically with $T_c = 69$ K and $T_c = 16$ K, respectively. The contrary is the case with pure EuTe which is an antiferromagnet of the MnO type with $T_N = 9.6$ K. EuSe is a metamagnet which orders at 4.6 K and exhibits various magnetic phases.

In the Eu chalcogenides the incorporation of *donors*, such as La, Gd, Ho, or the halogens⁴ produces an additional indirect exchange which manifests itself in a considerable increase of the paramagnetic Curie temperature. This additional magnetic exchange is ferromagnetic for all nondegenerate semiconducting Eu chalcogenides, independent on whether the spin lattice orders

ferro- or antiferromagnetically. On the other hand, this kind of doping results in a magnetically inhomogeneous material with the formation of large magnetized areas. The impurity electrons magnetically polarize a certain region near the donors, the size of which depends on the temperature, the applied magnetic field, and the concentration of donors. A manifestation of this magnetic inhomogeneity is the rounded peak of the magnetic specific heat as observed in EuO:Gd and EuS:Gd.^{3,5} In addition, doping in the order of a few percent can lead to chemical clustering of the dopant, which may even result in an "electronically amorphous" ferromagnet.⁶

Other investigations have shown that in materials containing anion or cation vacancies, such as ^{7,8} EuO_{1-x} and ⁹ Gd_{3-x}S₄ (where x denotes the vacancy concentration) a ferromagnetic exchange interaction exists owing to bound or localized electrons. EuO containing a deficiency of oxygen has been found to undergo a semiconductor-metal transition when passing through the Curie temperature. Interpretations^{7,8} are based on the model that two electrons are bound to the vacancy (F center) in the paramagnetic region owing to the joint action of a Coulomb interaction and a magnetic interaction. The latter comes about because the weaker bound electron loses energy in magnetically polarizing neighboring Eu spins. With the ordering of the spin lattice the magnetic part of the binding energy diminishes, so that the electron will become practically free leading to a metal-like conduction. In Gd₃S₄ containing Gd vacancies, a ferromagnetic component in the magnetization is reported⁹ in the otherwise antiferromagnetic material. The observed magnetization curves are thus

similar to those observed in doped EuTe.^{10, 11}

Since a doping-induced additional ferromagnetic exchange is more easily observed in an antiferromagnet, we have chosen EuTe for our investigation and have carried out several different experiments on differently doped samples. It has been shown that doping with Gd can lead to complications owing to a possible formation of vacancies and/or of Gd clusters.³ Furthermore, the magnetic $4f^7$ state of Gd^{3+} is about 9 eV below the Fermi level¹² in contrast to the $4f^7$ levels of Eu^{2+} which, in EuTe, are about 2 eV below E_F . Instead, the impurity electrons were introduced by doping in the anion lattice by substituting Te with I. Because the ionic radii of Te and I compare favorably, we believe that we have the highest probability to keep the spin lattice the same as in the undoped material.

As the physical properties are very sensitive to the impurity electron concentration and as this can vary strongly even within a given batch of crystals, it was found important that all investigations be done on the very same samples. Our measurements were primarily carried out on three different samples: an undoped sample labeled No. 384, which showed no signs of free charge carriers, neither in the optical absorption nor in the Faraday rotation; and two differently doped sample Nos. 399 and 829. The photoconductivity measurements were carried out on a different sample, however, of the same batch as crystal No. 399, and it is therefore labeled No. 399P. All doped samples were nondegenerate, exhibiting an activated carrier concentration, and were transparent in the red.

We present experiments giving direct evidence of the existence of ferromagnetic spin clusters (magnetic polarons). Here the experimental technique is primarily Faraday rotation, from which the magnetization was determined and the anomalously large wavelength-independent Faraday rotation owing to magnetic resonance was discovered.¹¹ We also report our observation of domain patterns, which further confirm the existence of spin clusters at low temperatures.¹³ Then we apply the concept of the magnetic polaron to explain further measurements of luminescence and photoconductivity. The samples are also characterized by their electrical transport parameters.

II. FARADAY ROTATION

The *interband* Faraday rotation of EuTe films has been investigated in the wavelength range from 0.2 to 0.6 μm and interpretations concerning the involved optical transitions have been given.^{14, 15} However, in the wavelength region *larger* than the

absorption edge (0.6–2.5 μm) the Faraday rotation of doped EuTe can consist of three independent terms: the interband Faraday rotation, intraband rotation owing to free charge carriers, and a term resulting from magnetic resonance. The interband Faraday rotation for energies smaller than that of the band gap is due to the tail in the dispersion curve resulting from the $4f^7-4f^65d$ transitions. The wavelength dependence of this rotation is accurately described by simple theory to be

$$\theta \sim M\lambda^2 / (\lambda^2 - \lambda_0^2)^2 \text{ rad m}^{-1}, \quad (1)$$

where λ_0 corresponds to the oscillator energy in a single oscillator model. Such a model for EuTe has also been found valid in a prior investigation concerning the refractive index.¹⁶ The interband Faraday rotation is directly proportional to the magnetization M , as has been verified by the excellent agreement between the paramagnetic Curie temperature determined through the interband Faraday rotation ($1/\theta$ vs T) and by direct magnetic measurements. In Fig. 1 the total Faraday rotation (FR) measured on three different samples is plotted versus the wavelength-dependent term of the interband rotation (for a physical characterization of the samples consult Table I). The pure sample No. 384 exhibits within experimental accuracy only an interband rotation, since the total FR, extrapolated to infinite wavelengths, intersects the ordinate in the origin. Both doped sample Nos. 339 and 829 exhibit, in addition, a FR owing to free electrons, which leads to a deviation from the straight line at long wavelengths proportional to λ^2 , in agreement with Drude theory.

The most striking result of our investigation is,

TABLE I. Magnetic-ordering temperatures and electric-transport data at 300 K for undoped and both doped EuTe samples.

SAMPLE	399	829	undoped
T_N [K]	9.6	9.6	9.6
θ [K]	+12	+14	-5
N [cm^{-3}]	4×10^{18}	6×10^{19}	0
μ [cm^2/Vsec]	66	11	
m^*/m (optical)	0.23	0.43	
$\Delta E(N)$ [eV]	0.02 ($T > 70\text{K}$)	0.02 ($T > 70\text{K}$)	
$\Delta E(\mu)$ [eV]	0.03 ($T > 70\text{K}$)		0.033 ($T \sim 70\text{K}$)

however, that in Fig. 1 the extrapolation of the total rotation less that owing to free charge carriers intercepts the ordinate at positive values. This indicates the superposition of a wavelength-independent term to the interband FR.¹¹ It is known that magnetic resonance can produce a wavelength-independent FR as has been found in many ferri- and ferromagnetic materials.¹⁷⁻²¹ These rotations are, however, smaller by an order of magnitude than the values we report.

In the case of magnetic resonance, the weak dispersion of the magnetic susceptibility results in a wavelength-independent FR for exciting frequencies much larger than the magnetic resonance frequency $\omega \gg \omega_0$. In *ferromagnetic* resonance the total magnetization is assumed to precess around the applied magnetic field under the action of the magnetic field of the light wave. This leads to a FR that is largely governed by the magnetization M ,

$$\theta_{\text{ferro}} = (\sqrt{\epsilon}/2c) \mu_0 \gamma M \text{ rad m}^{-1}, \quad (2)$$

where ϵ denotes the optical dielectric constant, μ_0 is the magnetic permeability, and γ is the gyromagnetic ratio. This FR typically takes values of about 100 deg/cm in many ferrites at full magnetic order,¹⁷⁻²¹ however, it should be considerably larger in the ferromagnetically ordering Eu chalcogenides. EuO is expected to show values up to about 790 deg/cm at magnetic saturation. An attempt to measure this contribution to the FR in, e.g., EuS failed, as this component could not be accurately separated from the very large interband FR at wavelengths up to 2.5 μm . In ferri- and possibly some antiferromagnetic materials *exchange* resonance can also lead to a wavelength-independent FR.^{18, 19, 22} Here the magnetization vector of one sublattice is taken to precess around the exchange field of the other sublattice. This leads to much higher resonance frequencies than in the case of ferromagnetic resonance owing to the larger exchange fields. Under the same condition that $\omega \gg \omega_0$, the FR owing to exchange resonance has been determined to be

$$\theta_{\text{ex}} = (\sqrt{\epsilon}/2c) \mu_0 |\gamma_1 \vec{M}_1 + \gamma_2 \vec{M}_2| \text{ rad m}^{-1}, \quad (3)$$

where \vec{M}_1 and \vec{M}_2 are the sublattice magnetization vectors.²³ The values of the rotation are, however, of the same magnitude as the ones owing to ferromagnetic resonance.

The wavelength-independent FR is strongly temperature dependent as shown in Fig. 2. The rapid increase at low temperatures indicates a strong dependence on magnetic order. It is not, however, proportional to the magnetization, since in the paramagnetic region it does not follow a Curie-

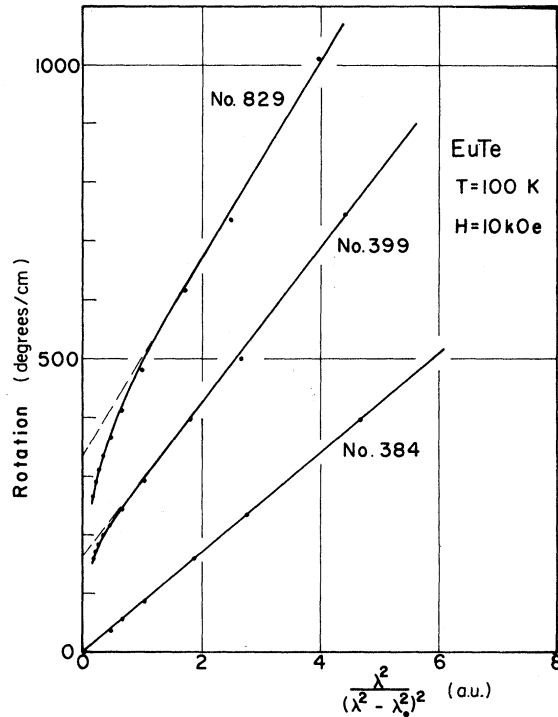


FIG. 1. Total measured Faraday rotation of an undoped sample No. 384 and two differently doped sample Nos. 399 and 829 plotted vs the wavelength-dependent term of the interband Faraday rotation.

Weiss relationship. Nor does it decrease for $T < T_N$, as does the magnetization, which is shown in the insert of Fig. 2. The strongest deviation from existing theories and experiments lies in the absolute value of this FR, which is an order of magnitude larger than expected. We thus have a quantitative and a qualitative discrepancy with Eq. (2) or (3). However, an explanation can be given assuming the existence of ferromagnetic spin clusters. Thus, the wavelength-independent FR is believed to originate from the magnetic resonance of these spin clusters in the exchange field of the magnetic sublattices of EuTe.¹¹ The wavelength-independent FR therefore depends primarily on the magnetization of such a spin cluster.

A ferromagnetic spin cluster is formed by the overlap of the wave functions of an impurity electron with neighboring Eu ions. Through the electron-ion *d**f*-exchange interactions, the 4*f*⁷ spins are coupled ferromagnetically to the spin of the *d* electron, thus forming at low temperatures ferromagnetically saturated regions^{24, 25} with a huge magnetic moment. Together with the magnetic interactions a Coulomb component in the binding energy of the impurity electron is assumed, which is also dependent on the dimensions of the

cluster and on a local lattice distortion (bound magnetic polaron). The degree of alignment of the Eu spins within a cluster is given by the nearest-neighbor spin-correlation function, which, even at room temperature, exhibits a nonzero value, as the wavelength-independent FR does not vanish at high temperatures. At low temperatures, the alignment towards saturation is apparent in the insert of Fig. 2 and saturation is practically achieved near 20 K, appreciably above $T_N=9.6$ K. The insert of Fig. 2 indicates that with the onset of long-range order (below T_N) a slight increase in the wavelength-independent FR and therefore in the cluster magnetization sets in. This can be interpreted either by an increase in size of the clusters owing to the increasing alignment of the spins neighboring the clusters, or by a magnetic interaction (coupling) between the clusters. The last argument would depend on the density of the clusters or the degree of doping and, indeed, such a further increase of the FR below T_N is not observed in the weaker doped sample No. 399. Therefore, we conclude that in this sample the interaction between the clusters is weaker than in the more heavily doped sample No. 829. In any case, we come to the conclusion that doped EuTe

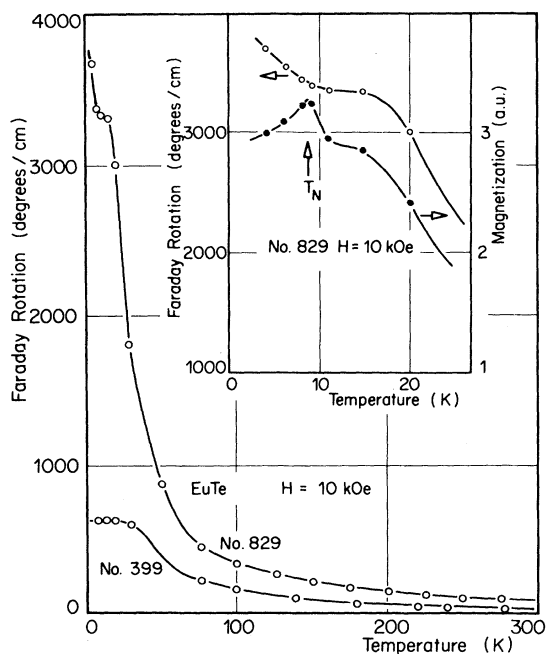


FIG. 2. Temperature dependence of the wavelength-independent Faraday rotation for two doped samples Nos. 399 and 829 at an applied magnetic field of 10 kOe. The insert shows the Faraday rotation and the magnetization of the more heavily doped sample No. 829 near T_N .

behaves as a magnetically inhomogeneous material with ferro- and antiferromagnetic regions. We must here remark that the antiferromagnetic regions need not possess strict antiferromagnetic order, as a deviation is expected resulting from the interactions between the ferromagnetic spin clusters.

The existence of ferromagnetic spin clusters is also apparent in the field dependence of the magnetization as displayed in Fig. 3. Again, the magnetization was determined from the interband FR with the magnetic field applied perpendicular to the flat samples. The measurement of the undoped sample No. 384 permitted the absolute calibration of the interband FR in units of μ_B , since it could be compared with well-known magnetic measurements.^{10, 26} Since the slope of the magnetization of, e.g., sample No. 829 in magnetic fields up to 2 kOe corresponds to the demagnetizing factor, which is unity in the applied geometry, we conclude that there exists a spontaneous magnetization in this sample for $T < T_N$ even in $H=0$, and that the magnetic moment of the clusters lie in the plane of the sample. This spontaneous moment is found to be $1.2\mu_B/(\text{Eu ion})$ for sample No. 829 and $0.4\mu_B/(\text{Eu ion})$ for sample No. 399 (see Fig. 3). Since the spin clusters are practically saturated at 8 K, they fully contribute to the increasing total magnetic moment for fields above 3 kOe. By comparing the total magnetization with the field dependence of the wavelength-independent FR, displayed in Fig. 4, it becomes evident that the latter is directly correlated only to the cluster magnetization or in other words to the spontaneous part of the total magnetization. Its rapid increase for $H < 2$ kOe is readily interpreted by the aligning of the separate ferromagnetic spin clusters parallel to the applied magnetic field. It remains to be said

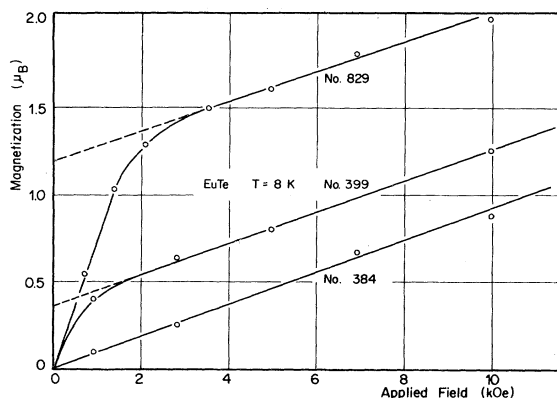


FIG. 3. Total magnetization vs applied magnetic field for both doped samples Nos. 399 and 829 compared with the undoped sample No. 384.

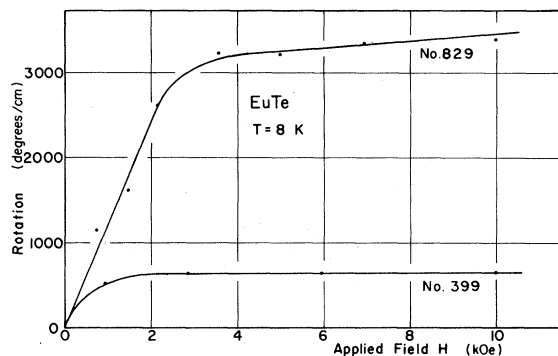


FIG. 4. Wavelength-independent Faraday rotation vs the applied magnetic field for both doped samples No. 399 and No. 829 at 8 K.

that the transition field $H_C \approx 70$ kOe from the spin-flop phase to the paramagnetic saturated phase is only slightly altered by impurity electrons.¹⁰ The wavelength-independent FR owing to the spin clusters is expected to vanish totally in fields above 70 kOe. Instead, one should only observe a wavelength-independent FR owing to ferromagnetic resonance.

It has been mentioned above that the higher doped sample No. 829 exhibits a spontaneous magnetization of $1.2\mu_B$, that is 17% of the saturation moment. This large spontaneous moment is caused by comparatively few impurity electrons, in the order of 0.001 of the atomic density. The ferromagnetic spin clusters therefore comprise a sizable number of Eu atoms. If we estimate the number of charge carriers at 10 K to be $2 \times 10^{18} \text{ cm}^{-3}$ (see Sec. V) and assume the clusters to be saturated, we find that each spin cluster contains roughly 500 Eu ions. When one uses the corresponding data of the weaker doped sample No. 399, assuming again total saturation within the clusters, one obtains clusters covering up to 2000 Eu ions. Hence, the size of the clusters is strongly dependent on the electron concentration.

In spite of the fact that we have used the simplest possible way of doping (see Sec. I), the appearance of ferromagnetic clusters seems to be common to all kinds of donors,^{10, 27} as they have been found also in EuTe crystals that were grown and doped using different techniques.

III. DOMAINS

The experimental results of Sec. II have been interpreted as originating from interactions of ferromagnetic spin clusters embedded in a more or less

antiferromagnetic spin lattice. In the following we report of our investigations on the influence of the impurity electrons on the domain pattern of sample No. 829 with the intention of further verifying the existence of the ferromagnetic spin clusters.¹³

Undoped EuTe is known to possess an antiferromagnetic order of the MnO type, where the spins lie parallel in (111) planes and thus form ferromagnetic sheets which are stacked in antiparallel sequence. As in MnO and NiO, antiferromagnetic EuTe is also expected to possess a deformation along the [111] axis owing to exchange striction, which renders these four directions birefringent and allows a direct observation of these domains (twin domains) with a polarizing microscope.^{28, 29} The boundaries between regions belonging to different contraction axes are called *T* walls. At least in the case of NiO it has been shown²⁸ that the antiferromagnetic axis passes continuously without alternation of direction through these walls. This is not the case for *S* walls (spin rotation boundaries), where the antiferromagnetic axis changes direction within a region of the same contraction axis. Previous observations of domains in the antiferromagnetic phase of EuSe and in undoped EuTe with a polarizing microscope revealed structures, which strongly differ from the *T* domains observed in MnO and NiO.³⁰ In these antiferromagnetic Eu chalcogenides the domains consist primarily of rather disordered patchy regions. In the present investigation *T* domain walls could for the first time also be observed similar to those found in MnO and NiO. Our samples were, however, unannealed, so that the domain boundaries were strongly pinned by imperfections and surface strains. In Fig. 5 the *T* walls were visible in the undoped sample No. 384 at 4.2 K and $H=0$. The polarizer was set 45° to the crystallographic [100] axes which are parallel to the edges of the photograph. No analyzer was used. A magnetic field of 3 kOe applied perpendicular to the flat sample reduced the number of *T* walls. *T* domain walls could also be observed in the strongly doped sample No. 829, however, they did appear much less frequently. This confirms the observation of the foregoing section that this sample is still primarily an antiferromagnet despite of the existing strong spontaneous magnetic moment.

To compare the domain pattern of the doped with the undoped sample, both crystals were mounted side by side and were simultaneously observed with transmitted monochromatic light using a polarizing microscope. In Fig. 6(a) the domain pattern of the doped sample No. 829 (upper-half) and of the undoped crystal No. 384 (lower-half) are displayed at 4.2 K and $H=0$. The gap between the crystals appears black, since polarizer and

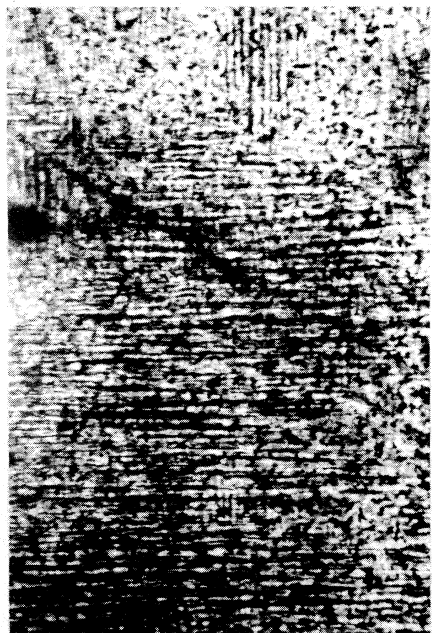


FIG. 5. T -domain boundaries in the undoped EuTe sample No. 384 at 4.2 K and $H=0$. The domain walls consist of the dark streaks parallel to the edges of the photograph which are again parallel to the crystallographic [100] axes. The polarizer was set at 45° to a [100] axis. No analyzer was used.

analyzer were crossed. Both analyzer and polarizer were set parallel to a [100] direction. As is visible in Fig. 6(b) a magnetic field of 3 kOe applied *parallel* to the light beam causes the domain picture in the doped sample to vanish, however, leaving the domain pattern in the undoped sample practically unaltered. Not only do the domains disappear in crystal No. 829, but the transmitted light becomes strongly depolarized. The remaining spots and streaks are produced by scratches and surface roughness owing to polishing. This loss of contrast owing to the depolarization of the light is very similar in its effect to the case of EuSe between 2.8 and 4.6 K, where a magnetic field induces a transition into a ferromagnetic state. In EuSe the antiferromagnetic domain pattern vanishes owing to the formation of optically not resolvable ferromagnetic domains. Similarly in doped EuTe the applied magnetic field aligns the ferromagnetic spin clusters parallel to the light beam. The depolarization of the light passing through the doped crystal can thus be explained by the individual Faraday rotation of the aligned spin clusters, which are statistically distributed and of random size. No depolarization occurs at $H=0$, since the directions of the magnetic moments of the spin clusters lie within the plane of the flat sample owing to the demagnetization (as argued in the



(a)



(b)

FIG. 6. Domain pattern in the undoped sample No. 384 (lower-half) and in the heavily doped sample No. 829 (upper-half) at 4.2 K. Polarizer and analyzer were set perpendicular to each other and parallel to a [100] axis: (a) $H=0$, (b) $H=3$ kOe. The magnetic field was applied perpendicular to the plane of the samples. The spots and streaks in the upper half are owing to scratches and surface strains.

previous section). The above interpretation is further confirmed by the fact that little change in the domain pattern occurs with magnetic fields up to 10 kOe applied *perpendicular* to the light beam in the plane of the samples. In this configuration depolarization can only occur owing to the Cotton-Mouton effect, which would produce elliptically polarized light. As is verified by experiment this effect is negligible. Light scattering also can not account for the described depolarization, because then it would be largely independent of the externally applied magnetic field. It must further be noted that the depolarization also occurs at temperatures slightly above T_N , from which we can again conclude that ferromagnetic spin clusters can be stable above the Néel temperature. This is consistent with the interpretation of the wavelength-independent Faraday rotation, which saturates at about 20 K.

With our method of differential observation of the domain pattern of an undoped and a doped sample it was also possible to detect a slight shift in the Néel temperature induced by the magnetic interactions of the impurity electrons. Thus the doped sample exhibited a Néel temperature of about 0.1 K lower than that of the pure sample. Such small shifts easily escape direct measurements. It was further observed that the ordering temperature of the doped sample was less sharp. This conclusion is derived from a more gradual decrease in contrast of the domain pattern with rising temperature compared with that of the undoped sample. Simple magnetic measurements have not been able to reveal a change of T_N owing to the presence of charge carriers.¹⁰

The ferromagnetic spin clusters have been determined to cover approximately 500 Eu ions for the higher doped sample, and are, therefore, of course, too small to be resolved with our microscope. Moreover, because of statistical fluctuations, we believe that at all temperatures the observation of spin clusters even with the best magnification should be impossible. As the impurity electrons are most likely to be statistically distributed, the ferromagnetic component of the substance is taken to be unstable in size and space. The coexistence of ferromagnetic and antiferromagnetic regions within the identical sample implies that EuTe weakly doped with impurity electrons should be labeled a "mixed magnetic" material. Based on the preceding experimental results the concept of ferromagnetic spin clusters (bound magnetic polarons) in nondegenerate EuTe seems well established and must therefore be taken into account when describing further effects such as the electrical transport properties, the luminescence, and the photosensitivity.

IV. LUMINESCENCE AND PHOTOCONDUCTIVITY

Earlier measurements of the photoluminescence in the Eu chalcogenides have revealed that the spectral position of the emission band and the quantum yield are strongly dependent on the magnetic order.^{31, 32} It is for this purpose that we have employed this experimental technique together with the photoconductivity to investigate the *local* magnetic order introduced by the impurity electrons in the sample Nos. 399 and 829 for temperatures between 4.2 and 300 K.

In the Eu chalcogenides photoluminescence is produced by the radiative recombination of a thermalized electron from the lowest conduction-band edge to the well localized $4f$ states of a photoionized Eu^{3+} ion. It has been shown for the special case of the undoped Eu chalcogenides that the quantum yield of the luminescence is large when both hole and excited electron are localized and close to each other with overlapping wave functions. This is so, because in the luminescent process of these materials no foreign activator is involved, and the excited electron (Franck-Condon mechanism) recombines with its own hole. In the above scheme it is obvious that, on the other hand, the photoconductivity of optically excited charge carriers is very poor when the carriers are localized, since photoconductivity is large only for high mobility electrons.^{31, 33, 34} Therefore luminescence and photoconductivity are competing mechanisms in the undoped Eu chalcogenides.

It has also been found that the amount of localization of the optically excited electron strongly depends on the type and degree of magnetic order. In the case of the ferromagnets EuO and EuS for $T \ll T_c$ the photoexcited electron is in a spin polarized conduction band of mostly d character and not localized. Therefore the luminescence is completely quenched and the photoconductivity is large. On the other hand, in antiferromagnetic EuTe for $T \ll T_N$ the photoexcited electron (s_{el}, r_{el}) is interacting with neighboring Eu spins (S_{ion}, R_{ion}) by means of the exchange interaction $J(r_{el} - R_{ion})s_{el}S_{ion}$, trying to align these Eu spins in parallel. This is in competition with the interatomic Heisenberg exchange $J_{ij}S_iS_j$ which tries to orient the Eu spins antiparallel. The result is a loss in mobility of the photoexcited electron and as a consequence a large luminescence and a disappearance of the photoconductivity.³⁵

In the paramagnetic region the luminescence and the photoconductivity are present at an intermediate level. That is, photoexcited electrons become more and more localized with decreasing temperature because the electrons magnetically polarize the thermally disordered neighboring Eu

spins and thus create magnetized microregions. At temperatures above 50 K the luminescence is quenched in all Eu chalcogenides owing to thermally induced delocalization of electrons and increasing radiationless transitions. Initial measurements of the luminescence on doped EuTe have already been carried out by P. Streit (Laboratorium für Festkörperphysik) but definite results could only be obtained after serious refinement of the apparatus. The emitted light was gathered along a different optical axis than the incident radiation. This allowed a strong reduction of scattered light of the exciting frequency. Furthermore, the wavelength of the exciting light was selected by a series of optical filters and the fluorescent spectrum was analyzed with a double monochromator in conjunction with another optical filter to absorb stray light. The luminescent light was detected with a cooled photomultiplier. The samples were *not* pulverized. Only with this arrangement was it possible to detect the very weak luminescence of the doped samples up to 300 K.

In Fig. 7 the relative intensity of the maximum in the luminescence emission band is displayed versus temperature for both doped samples at $H=0$ and $H=9.5$ kOe. In the insert of the same figure the behavior of the undoped sample is also displayed. The luminescence yield of sample

No. 399 is found to be considerably smaller than that of an undoped sample, and it is obvious that in the more heavily doped crystal No. 829 the luminescence is heavily quenched. This general reduction in fluorescence yield with increasing impurity electron concentration is not primarily owing to an increase in the absorption, since the undoped and the doped sample No. 399 have very similar absorption coefficients in the spectral region of the luminescence emission band. Furthermore, the emission spectra in all three samples are found to be comparable with a bandwidth of about 0.2 eV. This suggests that in all three cases the radiative recombination occurs at the same center, namely, at the Eu ion.³² The poor fluorescence of the doped samples can, however, be explained by lattice distortions and inhomogeneities, which strongly increase radiationless recombinations owing to a relaxation of q -selection rules.

Generally the temperature dependence of sample No. 399 displays a mixed ferro- and antiferromagnetic behavior: the quenching of the luminescence yield below about 30 K is typical for a ferromagnet, while the increase of the yield below T_N is typical for an antiferromagnet. The wavelength-independent FR suggests that bound magnetic polarons and therefore, locally, a short-

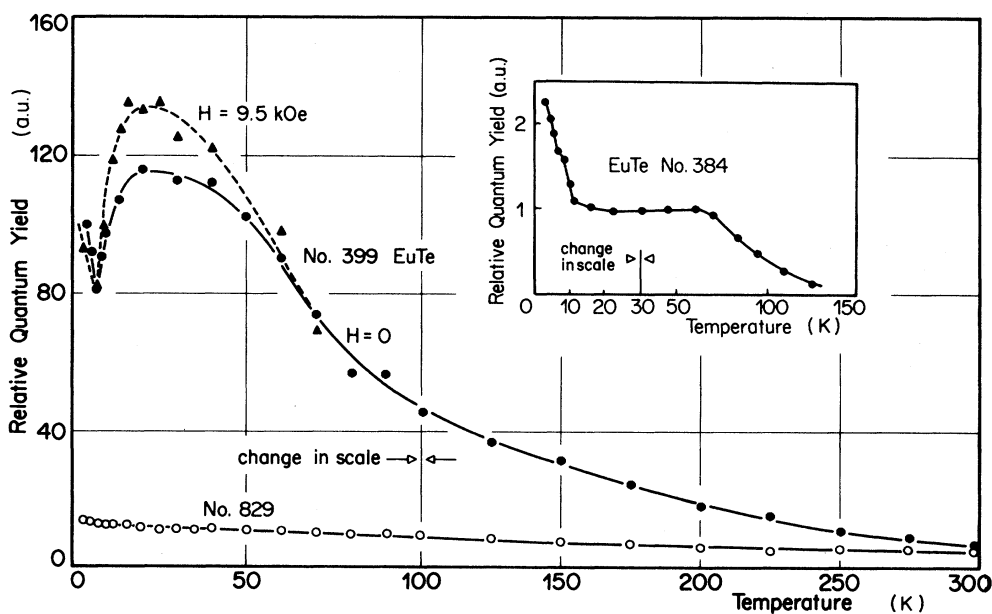


FIG. 7. Temperature dependence of the relative quantum yield of the photoluminescence for both doped samples Nos. 399 and 829 at $H=0$ and $H=9.5$ kOe. No field dependence for $H \leq 9.5$ kOe was observed in sample No. 829. Note the change in the temperature scale. In the insert the relative quantum yield of the photoluminescence is plotted for an undoped EuTe sample (Ref. 32).

range ferromagnetic order exist well above the magnetic ordering temperature. Electrons which happen to be optically excited within the region of such a spin cluster will become delocalized as the clusters approach magnetic saturation, owing to the local development of a highly spin-polarized conduction subband. The luminescence originating in the ferromagnetic clusters will thus be quenched for temperatures below about 30 K. It is quite interesting to realize that for a highly doped sample and low enough temperatures, the spin clusters become "black spots" with no light emission, which, however, are not stable in size and space. Thus at temperatures below 30 K the luminescence originates predominantly from the regions outside the clusters. Bearing this in mind, we conclude that the quenching of the luminescence below 30 K results from the loss of yield from the ferromagnetic clusters and from a ferromagnetic quenching outside the clusters as these are expected to interact and therefore distort the spin structure in the surrounding regions. At temperatures below T_N the long-range antiferromagnetic order outside the clusters which, however, contains a ferromagnetic component owing to the clusters, gives an increase in the luminescence yield as is found in undoped EuTe and is also shown in the insert of Fig. 7.

This model of a mixed magnetic structure is further confirmed by photoconductivity measurements.³⁶ We recall that the photoconductivity in the undoped Eu chalcogenides has generally been found to exhibit temperature and magnetic field dependence opposite in behavior from the luminescence.^{34, 35} In our mixed magnetic material the photoconductivity at very low temperatures will predominantly be carried by mobile excited electrons in the ferromagnetic clusters, whereas the contribution of electrons excited in the more antiferromagnetic regions would be negligible. We can thus explain the increase in photosensitivity for temperatures below 50 K, as displayed in Fig. 8, with the increasing alignment of spins in the clusters, which gradually become saturated. At still lower temperatures the photoconductivity in the regions outside the clusters becomes reduced owing to antiferromagnetic short-range order and for $T < T_N$ no photoconductivity is expected in the antiferromagnetic regions. A critical scattering term at T_N may be superimposed to explain the sharp minimum. That an applied magnetic field for $T < T_N$ increases the photoconductivity and decreases the photoluminescence can easily be explained by an increasing ferromagnetic component of the total magnetization as seen, e.g., in Fig. 3. Unusual for the Eu chalcogenides is the fact that a magnetic field enhances the lumines-

cence yield and decreases the photoconductivity for $T \gg T_N$. This anomalous behavior suggests that the magnetic field increases the localization of the excited electrons. An explanation can be proposed on the basis of a positive magnetoresistance effect, which has been established for the degenerate Eu chalcogenides.³⁷ Our measurements verify that this effect also occurs in nondegenerate samples. Thus we conclude that owing to the different origin of the luminescence and the photoconductivity in our doped samples, both luminescence and photoconductivity for the first time show a *similar* behavior in the temperature dependence.

A last remark shall be made concerning the shift of the luminescence emission band with temperature and magnetic field. Generally the Stokes shift of the luminescence emission band in the Eu chalcogenides is determined by three terms, the elastic, the electronic, and the magnetic relaxation of the thermalized photoelectron in the vicinity of the luminescence site.^{31, 32} It has been shown that the temperature and the magnetic-field dependence of the frequency of the emission band at low temperatures is largely governed by the magnetic relaxation.³² This magnetic relaxation is dependent on the local magnetic order at the luminescence site. Since the excited electron always has the tendency to couple neighboring spins parallel, the magnetic relaxation always exists and is strongest in the ferromagnets and weakest in the antiferromagnets. Thus ferromagnetic order gives rise to a red shift of the luminescence emission band and antiferromagnetic order to a blue shift. The spectral position of the luminescence band for the weakly doped sample No. 399 is displayed in Fig. 9. With decreasing temperature the luminescence shifts to the blue when cooling to about 30 K. This can possibly be explained by a thermal process. As argued above, the lum-

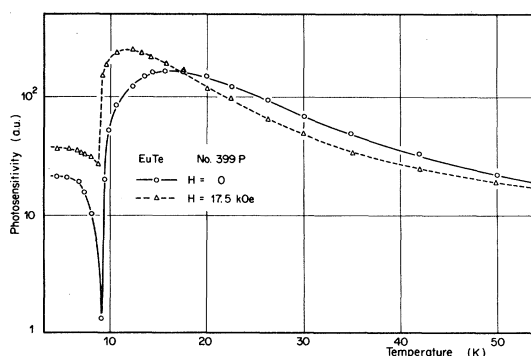


FIG. 8. Temperature dependence of the photoconductivity of a doped EuTe sample No. 399P for $H = 0$ and $H = 17.5$ kOe.

inescence for $T < 30$ K predominantly occurs in the regions outside the ferromagnetic clusters. That this region outside of the clusters does not order strictly antiferromagnetically, but that a ferromagnetic component also exists owing to the interactions between the clusters, is in fact proven by the red shift of the emission band between about 30 K and T_N . This stands in contrast to undoped EuTe, where the emission band shifts to the blue in the same temperature range as seen in the insert of Fig. 9.

V. ELECTRICAL TRANSPORT PROPERTIES

In order to better characterize our samples and to determine the conduction mechanisms we have evaluated the electrical transport data with a method which has previously been employed successfully for doped EuO. Details of this method are found elsewhere.³ In short, the carrier concentration N , the optical mobility μ , and the effective mass m^* were determined by solving a set of three independent equations, which are related to three separate measurements, namely, the Faraday rotation and optical absorption owing to free charge carriers and reflectivity measurements near the plasma edge. The dc values of the mobility were evaluated by extrapolating the frequency-dependent scattering time to a frequency corresponding to kT . The law from which this extrapolation was carried out was obtained from the frequency dependence of the optical absorption. This method of extrapolation is partially justified by the excellent agreement between our values and those determined through Hall and resistivity measurements in similarly doped samples.²⁷ The electrical transport data and the magnetic ordering temperatures for both doped samples and the pure sample are

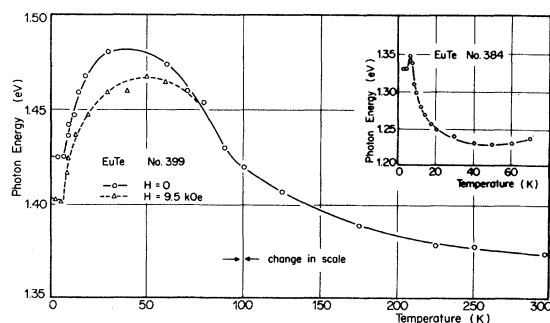


FIG. 9. Temperature dependence of the spectral position of the maximum in the luminescence quantum yield for the doped sample No. 399 at $H = 0$ and $H = 9.5$ kOe. Note the change in the temperature scale. In the insert the spectral position of the luminescence emission band is displayed for an undoped EuTe sample (Ref. 32).

listed in Table I. The temperature dependence of the carrier concentration was determined using a temperature-independent effective mass, as the reflectivity measurements in the far infrared could only be carried out at room temperature. None the less, both doped samples for $T > 70$ K exhibit activation energies in N , which are identical within experimental accuracy, $\Delta E(N) = 0.02$ eV, and are very similar to that found in doped EuO, $\Delta E(N) = 0.017$ eV.³ Thus the free charge carriers measured by the optical absorption and Faraday rotation are activated from shallow donors. The dc mobility of the weakly doped sample No. 399 is found to exhibit an activation energy $\Delta E(\mu) = 0.03$ eV, which is very similar to that found in an undoped sample through photoconductivity measurements at $T > 70$ K.³⁴ Here a value of $\Delta E(\mu) = 0.033$ eV was found. From this we conclude that the activation energy of the mobility is not typical for the iodine dopant. Furthermore, the dc mobility exhibits an activation energy, which is larger than that of the carrier concentration. This implies that the activation energy in the hopping mobility is purely of magnetic origin, and that hopping does not occur between impurity states. This same conclusion has also been derived from the transport data of doped EuO.³ For $T < 50$ K the transport data of our doped EuTe samples could only be estimated, as the damping g was larger than the light frequency ω in this temperature range.

VI. CONCLUSION

In this paper we have shown the powerful techniques of optical and magneto-optical investigations to obtain information concerning additional exchange mechanisms incorporated by doping of magnetic semiconductors.

The FR together with optical absorption and reflectivity measurements not only yielded paramagnetic Curie temperature, Néel temperature, and total magnetization, but also the spontaneous magnetization of spin clusters, a new magnetic resonance effect, and the number of charge carriers, their mobility and activation energies.

Owing to their different origin inside or outside the spin clusters, luminescence and photoconductivity gave further insight into the micromagnetic behavior of our magnetically inhomogeneous system. The observation of differential domain patterns made it especially clear that our material was not an overall ferrimagnet, but that depolarization of light in low fields had its origin in magnetic inhomogeneities and spin fluctuations.

As a consequence, doped nondegenerate EuTe must be termed a "mixed magnetic" material, which at low temperatures consists of ferromag-

netically saturated spin clusters, comprising between 500 and 2000 Eu ions, and a more or less antiferromagnetic region outside the clusters. The best argument that the main part of the material is not purely antiferromagnetic is given by the color shifts of the emission spectrum.

It is thus very remarkable that the early ideas of an itinerant electron magnetism described by the Ruderman-Kittel-Kasuya-Yoshida interaction^{1,2} and introduced by doping of magnetic semiconductors have not been found justified in more careful experiments. In EuO doped with Gd magnetic cluster formation has been found and theories concerning this magnetic behavior have been

developed.^{3,6,25} The concept of bound magnetic polarons as introduced by Torrance *et al.*⁸ also proved to be especially useful for our purposes, however, the possibility of self-trapped magnetic polarons, particularly in antiferromagnets, having *f-d* exchange and *d*-character conduction bands, can also not be abandoned.

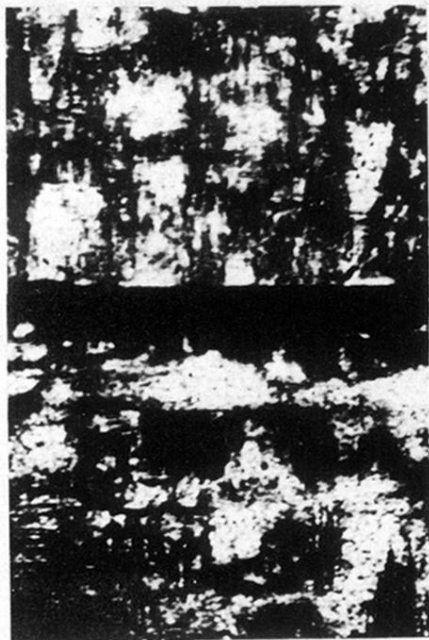
ACKNOWLEDGMENTS

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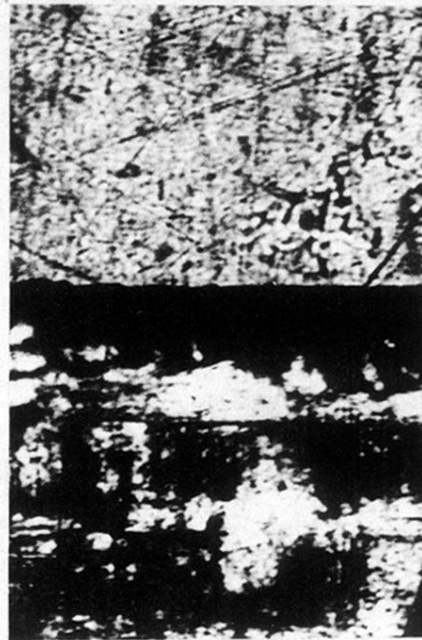
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FIG. 5. T -domain boundaries in the undoped EuTe sample No. 384 at 4.2 K and $H=0$. The domain walls consist of the dark streaks parallel to the edges of the photograph which are again parallel to the crystallographic $[100]$ axes. The polarizer was set at 45° to a $[100]$ axis. No analyzer was used.



(a)



(b)

FIG. 6. Domain pattern in the undoped sample No. 384 (lower-half) and in the heavily doped sample No. 829 (upper-half) at 4.2 K. Polarizer and analyzer were set perpendicular to each other and parallel to a [100] axis: (a) $H=0$, (b) $H=3$ kOe. The magnetic field was applied perpendicular to the plane of the samples. The spots and streaks in the upper half are owing to scratches and surface strains.