Magnetic Exchange Interaction in the System GdP-GdS

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(Received 28 November 1977)

Magnetic susceptibility and magnetization have been measured for a series of GdP and GdS compounds having various stoichiometries and mixing ratios. Also the free-carrier concentration has been determined for all compositions. One clearly observes a Ruderman-Kittel-Kasuya-Yosida oscillation with positive and negative Θ values being superimposed on an antiferromagnetic superexchange and possibly a dipolar interaction. All compounds are antiferromagnets.

GdP and GdS belong to a group of materials which have at least two systems of electrons contributing to the magnetic exchange: localized $4f$ electrons and free itinerant carriers. In general it is very difficult to estimate the relative amount of importance to the magnetic properties of either electron system, especially if relevant experimental data are missing. Thus GdP has been claimed to be antiferromagnetic because of a Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange of the free carriers, their concentration being *postulated* to be $N_{el}/N_{Gd} = 1.4$.[1] [N_{el} is the free carrier; N_{Gd} is the Gd concentration (cm^{-3}).] In an analysis of crystal-field effects on nitrides and phosphides by means of inelastic neutron scattering Birgeneau *et al.*[2] also conclude that phosphides have N_{el}/N_{cation} near 1. With these high carrier concentrations the RKKY interaction would indeed yield antiferromagnetism in agreement with the experimental observations.[3,4] GdS, which in the stoichiometric case has $N_{el}/N_{Gd} = 1$,[5,6] was also claimed to be antiferromagnetic because of the RKKY interaction,[7] but Campagna, Kaldis, and Siegmann[8] believe they have shown by spin-polarized photoemission that the free carriers couple ferromagnetically. On the other hand, the stoichiometry variation of GdS and the concomitant change in N_{el}/N_{Gd} has given evidence for increasing antiferromagnetic exchange with increasing carrier concentration.[9] It thus comes as no surprise that Sakurai *et al.*[10] in a theoretical analysis of experimental magnetic data of pnictides and chalcogenides reach the conclusion that the RKKY interaction alone can in no case account for the magnetic properties of the material.

The various problems and contradictions pointed out above and the lack of dependable experimental data were the motivation to investigate the GdP-GdS system and correlate for the first time the magnetic properties with the measured number of free carriers. Such a task has been undertaken before in the systems EuSe-GdSe and EuSe-LaSe by Holtzberg *et al.*,[7] but replacement of the magnetic cation shifts the $4f^7$ level from about 1 eV below the Fermi level E_F in EuSe to about 7 eV below E_F in GdSe and thus introduces more and more antiferromagnetic superexchange.[11] Replacing Eu with La dilutes the magnetic system and is thus also not conclusive. In the compound series GdN-GdO,[12] nitrogen can only be replaced by oxygen to an extent of 12%. In addition, no relation of magnetic properties with the presumably drastically changing carrier concentration has been performed since the latter has not been evaluated. Also, in the alloy systems $GdAs_{1-x}S_x$ and $GdSb_{1-x}Te_x$[13] the electron concentration has not been measured, but instead the hypothetical value of Darby and Taylor[1] of $N_{el}/N_{Gd} = 1.4$ has been taken for granted for GdAs and GdSb, using linear interpolations for alloys between $N_{el}/N_{Gd} = 1.4$ and 1 for the end members of the series. In the meantime, it has been shown that another arsenide, SmAs, has N_{el}/N_{Gd} of only 0.045.[14,15] The system GdP-GdS is expected to be more suitable since the compounds are isomorphic fcc and the lattice constants of the end members are not very different (see Table I); also, in GdP and in GdS the $4f^7$ level is about 7 eV below E_F and the crystal-field splitting of the $5d$ conduction band is about the same (Table I)[14,16] except that GdP is more covalent than GdS, resulting in a diminishing gap between valence p bands and conduction d bands in GdP.[11] Besides, variation of stoichiometry, instead of alloying, keeps the lattice parameter constant near the end members of the series (see Table I), and so confusions as to the magnetic properties depending on Gd distance or free-carrier concentration can largely be avoided. In the GdP-GdS system, N_{el}/N_{Gd} could be changed between 0.07 and 1.2 either by variation of the stoichiometry or by suitable alloying.

TABLE I. Chemical and physical parameters of the GdP-GdS system. a_0 is the lattice constant, Δ the crystal-field splitting $5dt_{2g}$-$5de_g$, N_{el} the free-carrier concentration. N_{el}/N_{Gd} the relative free-carrier concentration, Θ the paramagnetic Curie temperature, T_N the Néel temperature, J_1 the nearest-neighbor exchange parameter, and J_2 the next-nearest-neighbor exchange parameter.

	a_0 (Å)	Δ (eV)	N_{el} (cm^{-3})	N_{el}/N_{Gd}	Θ (K)	T_N (K)	J_1 (K)	J_2 (K)
$GdP_{1.0}$	5.728	1.8	1.5×10^{21}	0.07	0	15.2	+0.12	−0.24
$GdP_{0.994}$	5.728	1.8	2.0×10^{21}	0.095	+2	15.2	+0.14	−0.24
$GdP_{0.934}$	5.720	1.8	2.4×10^{21}	0.11	+22	15.2	+0.29	−0.24
GdP_x	5.709	1.7	5.0×10^{21}	0.23	+17	16.2	+0.26	−0.26
GdP/GdS	5.655	1.6	8.5×10^{21}	0.38	−46	25	−0.16	−0.40
$Gd_{0.94}S$	5.5606	1.6	2.12×10^{22}	0.91	−97	38	−0.41	−0.71
$GdS_{0.94}$	5.5505	1.6	2.63×10^{22}	1.13	−102	42	−0.43	−0.76
$GdS_{0.88}$	5.555		2.8×10^{22}	1.2	−115	44	−0.48	−0.87

The experiments, which have been performed on eight single-crystalline samples with different composition, consisted of lattice-constant, chemical-analysis, phase-purity, optical reflectivity, magnetization, and susceptibility measurements. The reflectivity of all samples shows a pronounced edge due to the plasma resonance of the free carriers. Near this edge the reflectivity rises from a minimum of a few percent to about 100% with decreasing photon energy. The position in energy of this edge is between about 3.4 eV for the GdS compounds and 0.4 eV for the GdP compounds. After a suitable decomposition of intraband and interband transitions, described in detail elsewhere,[6,14] the unscreened plasma energy ω_p of the free carriers could be determined. It is connected with the free-carrier concentration N_{el} by

$$\omega_p^2 = 4\pi N_{el} e^2/m_{opt}^*. \quad (1)$$

The optical effective mass m_{opt}^* has been determined on stoichiometric GdS by a comparison of Hall-effect data[5] and plasma resonance[6] and has been found to be $1.3m$. For SmAs, similar to GdP, it has been found to be $1.2m$.[14,15] Thus from the optical determination of the plasma resonance we obtain N_{el} for all compounds, which can now be correlated for the first time with the magnetic data.

At first it remains to be stated that stoichiometric GdP has $N_{el} = 1.5\times10^{21}$ cm^{-3}, corresponding to $N_{el}/N_{Gd} = 0.07$ and the GdP with the lowest carrier concentration ever observed has $N_{el}/N_{Gd} = 0.046$.[14] Estimated relative concentrations near 1 or larger,[1,2] therefore, are far from reality. An RKKY interaction with the experimentally observed low carrier concentrations now yields a ferromagnetic contribution in contrast to Ref. 1. This can indeed be proven experimentally by plotting the paramagnetic Curie temperatures Θ against the relative concentration N_{el}/N_{Gd} (Fig. 1 and Table I). With increasing carrier concentration Θ increases from 0 to +22 K, passes through a maximum (in this connection it is of interest to note that Iandelli[17] reports a $\Theta = +40$ K for GdP with unknown stoichiometry and carrier concentration), and finally decreases to −115 K for a nonstoichiometric GdS composition.

Now we may consider the magnetic behavior of GdP with no free carriers. The extrapolation of the curve in Fig. 1 towards $N_{el}/N_{Gd} \to 0$ clearly in-

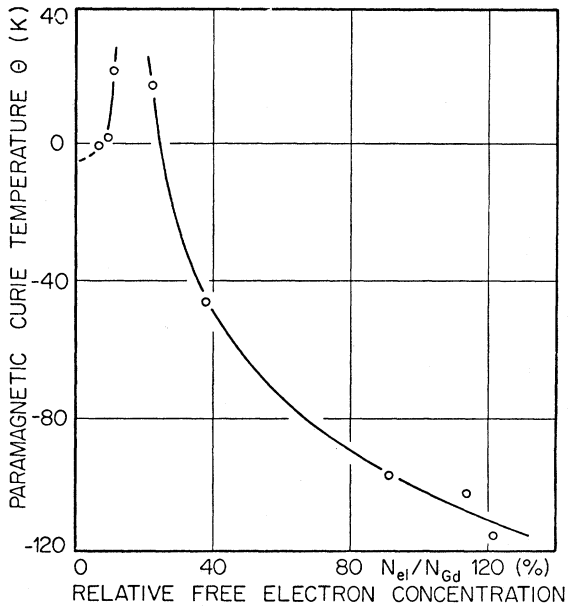

FIG. 1. Paramagnetic Curie temperature vs relative free-electron concentration of GdP, GdP/GdS, and GdS.

dicates a negative Θ between about -10 and -15 K. Thus in the absence of free carriers GdP is an antiferromagnet either due to an *fd* superexchange[11] or a magnetic dipole interaction, which can be shown to have a similar magnitude. The free carriers superimpose an RKKY interaction with its typical oscillatory behavior. This is supported by the fact that the first three compositions of GdP (Table I) have practically the same lattice constant and Gd separation, and thus superexchange and dipolar interaction are not changing. The composition labeled GdP_x, on the other hand, has a somewhat reduced Gd separation compared to the others and thus Θ should rise from the point of superexchange[18]; however, experimentally the contrary is the case, which must be associated with the drastic change in the carrier concentration.

Although the magnetic structure of GdP is not known because of its high absorption cross section for neutrons, it is most likely that it is type-II antiferromagnetic just as in GdS.[13] This is also suggested by its similarity with EuTe. Thus the magnetization for stoichiometric GdP increases linearly with field and it reaches at 1.7 K about $7\mu_B$ for fields larger than $H_c = 95$ kOe.[19] Above this field the spins are aligned ferromagnetically (Fig. 2). A significant difference is observed for $GdP_{0.934}$ where apparently the linear increase with field is superimposed with a part showing ferromagnetic saturation (Fig. 2). However, we note that in this sample even at 100 kOe complete saturation of the total magnetization has not yet been achieved. The initial slope of the magnetization of the ferromagnetic part corresponds to about the inverse of the demagnetizing factor, thus we conclude that there exists a spontaneous magnetization in this sample even in $H \to 0$. This spontaneous moment is found to be about $0.78\mu_B$ per Gd ion. Again we note a similarity with doped EuTe[20] where this effect has been explained with ferromagnetic spin clusters. However, in EuTe the doping was with about 6×10^{19} cm^{-3} free carriers—much less than in $GdP_{0.934}$ ($N_{el} = 2.4\times10^{21}$ cm^{-3})—thus spin clusters appear unlikely in GdP. For the GdP_x compound with even more electrons, the magnetization curve is rounded from the beginning and it always stays below the curve for $GdP_{0.934}$, having reached $5.9\mu_B$ per Gd ion at 100 kOe (Fig. 2). The GdP/GdS alloy, on the other hand, shows again a linear increase with field (Fig. 2), just as is the case for the GdS compounds.

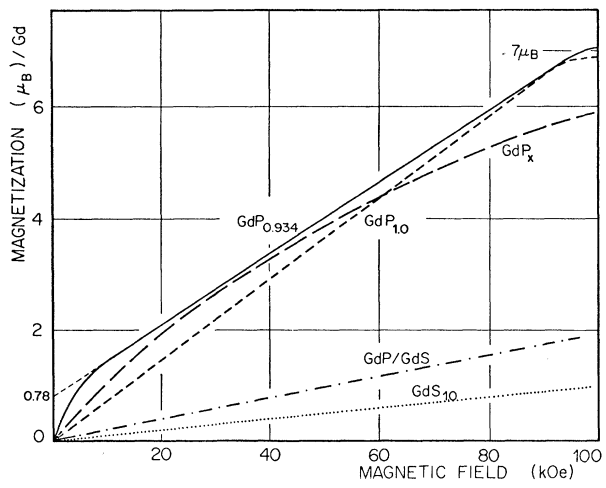

FIG. 2. Magnetization per Gd ion of GdP, GdP/GdS, and GdS as a function of magnetic field at 1.7 K.

Assuming the type-II antiferromagnetic structure for the whole GdP-GdS series, we can perform a simple molecular-field analysis and compute the nearest-neighbor J_1 and next-nearest-neighbor J_2 exchange parameters, so that

$$\Theta = \tfrac{2}{3}S(S+1)(12J_1 + 6J_2) = 126J_1 + 63J_2,$$
$$T_N = \tfrac{2}{3}S(S+1)(-6J_2) = -63J_2, \qquad (2)$$

where T_N is also collected in Table I. Just like Θ, J_1 exhibits an oscillatory behavior for the GdP-GdS series. With the help of Eq. (3), which is an estimate of the critical field necessary for saturation[21]

$$q\mu_B H_c(T \to 0) \simeq -84(J_1 + J_2)k_B, \qquad (3)$$

we can derive a saturation field of about 350 kOe for the GdP/GdS compound and about 700 kOe for the GdS compositions in agreement with extrapolations from the experimental curves (Fig. 2).

In conclusion, it can be said that the GdP-GdS series is the magnetic system which comes closest to the ideal of only filling electrons into an initially empty conduction band and studying the additional exchange interactions. In this case the electron concentration could be varied in the range $0.07 < N_{el}/N_{Gd} < 1.2$, i.e., by a factor of nearly 20. It is obvious, regarding Fig. 1, that GdP is an antiferromagnet because of its *fd* superexchange or dipolar magnetic interaction, and the free carriers superimpose a ferromagnetic contribution not strong enough to make the compounds a ferromagnet as a whole. On the other hand, in GdS superexchange as well as the RKKY interaction go in the same direction as an antiferromagnetic exchange.

We are most grateful to Dr. O Vogt for permission to use this apparatus and for valuable discussions. We also wish to express our gratitude to K. Mattenberger for performing the magnetic measurements and to J. Müller for measuring the optical properties of the samples. The support of the Swiss National Science Foundation is gratefully acknowledged.

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