to earlier experimental work.

[7]We use here the notation proposed by R. B. Griffiths, Phys. Rev. B 7, 545 (1973).

[8]For a summary of previous work on DyAlG see D. P. Landau, B. E. Keen, B. Schneider, and W. P. Wolf, Phys. Rev. B 3, 2310 (1971); W. P. Wolf, in "Magnetism and Magnetic Materials—1974," AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (to be published), p. 255.

[9]We should also note recent measurements of the "transparent magnetic circular dichroism" in $FeCl_2$ by J. A. Griffin, S. E. Schnatterly, Y. Farge, M. Regis, and M. P. Fontana, Phys. Rev. B 10, 1960 (1974). This would seem to be a very promising technique for TCP investigations, but no measurements of any TCP exponents using this technique have been reported as yet.

[10]J. F. Dillon, Jr., E. Yi Chen, N. Giordano, and W. P. Wolf, Phys. Rev. Lett. 33, 98 (1974).

[11]J. F. Dillon, Jr., E. Yi Chen, and H. J. Guggenheim, in "Magnetism and Magnetic Materials—1974," AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (to be published), p. 200; J. F. Dillon, Jr., E. Yi Chen, and W. P. Wolf, in Proceedings of the International Conference on Magnetism, Moscow, U. S. S. R., 22–28 August 1973 (to be published).

[12]M. Blume, L. M. Corliss, J. M. Hastings, and E. Schiller, Phys. Rev. Lett. 32, 544 (1974); R. Alben, M. Blume, L. M. Corliss, and J. M. Hastings, Phys. Rev. B 11, 295 (1975).

[13]V. J. Emery, Phys. Rev. B 11, 3397 (1975); D. R. Nelson and J. Rudnick, Phys. Rev. Lett. 35, 178 (1975).

Measurement of Spin-Flip-Raman-Scattering Cross Section and Exchange Effects for Donors in CdS by Faraday Rotation

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The simple connection between spin Faraday rotation and spin-flip-Raman-scattering (SFRS) cross section is used to deduce the SFRS cross section for donors in CdS from Faraday-rotation measurements. The Faraday rotation also reveals an antiferromagnetic exchange interaction between donors.

We have measured the Faraday rotation (FR) due to the donor spins in n-CdS at several different optical wavelengths and donor concentrations. These rotations become huge at near-resonant light excitation. In view of the very simple connection between the spin-flip-Raman-scattering (SFRS) cross section ($d\sigma/d\Omega$) and spin FR, which we express directly in terms of a "Raman dipole," one can thus determine the SFRS cross section by the measurement of FR. The latter is uncomplicated by the necessity for corrections for surface and bulk absorption, reflectivity, geometrical factors, etc., which trouble any cross-section measurement as evidenced by the orders-of-magnitude disagreement in $d\sigma/d\Omega$ quoted in the literature.[1,2] In addition, the near-resonant spin FR provides a very sensitive means of measuring interactions between electrons.

In a previous communication, we showed that for cubic symmetry, Raman scattering of a light field $\vec{E}_L \cos(\omega_L t)$ from any two time-reversed states $|a\rangle$ and $|b\rangle$ separated by a Zeeman energy $\hbar\omega_{ba}$ is conveniently represented by matrix elements between states $|a\rangle$ and $|b\rangle$ of an effective Raman dipole[3]

$$\vec{D}^{(2)} = \vec{\sigma}\times\vec{E}_L[\alpha\exp(-i\omega_L t)+\text{c.c.}] + [\beta\vec{E}_L\tilde{I}\exp(i\omega_L t)+\text{c.c.}]. \quad (1)$$

Here $\vec{\sigma}$ is the Pauli spin operator, $\tilde{I}$ is the unit matrix, and β and α are second-order matrix elements of the electric dipole operator $e\vec{r}$ of the type

$$\alpha = \sum_n \tfrac{1}{2} i \langle a|ex|n\rangle\langle n|ez|b\rangle/(E_n - E_a - \hbar\omega_L). \quad (2)$$

β is the usual polarizability associated with the dielectric constant and forward Rayleigh scattering. Spontaneous Raman scattering between $|a\rangle$ and $|b\rangle$ is given by the Raman electric dipole, $\langle b(t)|\vec{D}^{(2)}|a(t)\rangle$. By appropriate insertion of this off-diagonal dipole into the classical radiation formula, the spontaneous differential SFRS cross section is given by

$$(d\sigma/d\Omega)_{SF} = 4|\alpha|^2(\omega_L \mp \omega_{ba})^4/c^4. \quad (3)$$

However, in addition to the component of $\vec{D}^{(2)}$ connected with β which radiates at the unshifted frequency ω_L, there are additional diagonal components associated with α which give rise to a

dipole at ω_L but rotated 90° relative to the plane of polarization of the incident light, i.e.,

$$(D_{y,x}^{(2)})_{aa} \sim (+,-)\alpha\langle a|\sigma_z|a\rangle E_{x,y} \times \exp(-i\omega_L t), \quad (4)$$

where z is the direction of the external magnetic field along which light is propagating. This corresponds to a Faraday rotation. The net dipole produced will be proportional to $\langle b|\sigma_z|b\rangle + \langle a|\sigma_z \times |a\rangle = \langle \sigma_z \rangle$. The dipole at frequency ω_L gives rise to a volume polarizability $\alpha\langle \sigma_z\rangle N + \beta N$ or a dielectric constant for right- and left-circularly polarized light given by

$$\epsilon_\pm = 1 \pm 4\pi\langle \sigma_z\rangle \alpha N + 4\pi\beta N, \quad (5)$$

where N is the number of scattering centers per unit volume. The FR, φ, per length, l, along z is given by

$$\frac{\varphi}{l} = \frac{2\pi(n_+ - n_-)}{\lambda} \simeq \frac{8\pi^2 N\alpha}{n\lambda}\langle \sigma_z\rangle \quad (6)$$

where $\epsilon_\pm = n_\pm^2$ and $\frac{1}{2}(n_+ - n_-) \simeq n$, the index of refraction. Thus, the "spin" FR, φ/l, and the SFRS cross section in Eq. (3) involve the same second-order matrix elements α so that $(d\sigma/d\Omega)_{SF}$ may be simply expressed in terms of the spin FR by[4]

$$\left(\frac{d\sigma}{d\Omega}\right)_{SF} = \left(\frac{\varphi}{l}\right)^2 \frac{n^2}{N^2\langle \sigma_z\rangle^2\lambda^2}. \quad (7)$$

Linearly polarized light from an argon-ion laser at different wavelengths was passed through a single crystal of n-CdS with the beam direction collinear with the c axis and external magnetic field. The rotation of the plane of polarization of the light passing through the crystal was measured with a Polaroid analyzer. The crystal was immersed in liquid He or cooled by a flow of He gas at higher temperatures.

Figure 1(a) shows the FR, φ, for $\lambda = 4965$ Å measured in a sample of In-doped CdS with 7×10^{16} donors/cm^3. In this concentration range, the donor electrons are completely localized and $\varphi \sim \langle \sigma_z\rangle$ should saturate as a Brillouin function for spin $\frac{1}{2}$ with a g value of 1.79[3] appropriate to donors in CdS. That, in fact, it does not results from the presence of a temperature-independent component, η, not related to the spins, which is associated with interband transitions in the pure crystal.[5] This may be seen in Fig. 1(b) where $R = (d\varphi/dH)_{H=0}$ is plotted versus $1/T$, which gives an intercept for $T \to \infty$ corresponding to the temperature-independent rotation $a = d\eta/dH = 2.8$ deg/kG mm. The pure-crystal background is temperature independent over the range of temperatures for which data points are shown in Fig. 1(b) as confirmed by the fact that the points fall on a straight line. This is to be expected as the variation in band-gap energy, E_g, with temperature is insignificant compared to $E_g - \hbar\omega_L$. At 4880 Å this condition becomes more stringent and data points were taken only to 12 K. If η is now subtracted from φ in Fig. 1(a), $\varphi - \eta$ is fitted by the above mentioned Brillouin function to a few percent.

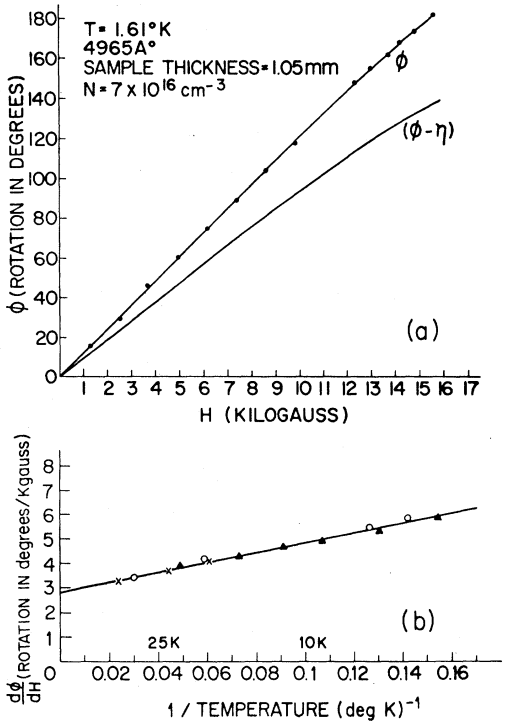

FIG. 1. (a) Field dependence of the observed FR, φ, at 4965 Å and of $\varphi - \eta$, the spin FR obtained by subtraction of the temperature-independent part η derived as described in the text. (b) Temperature dependence of $d\varphi/dH$ used to obtain η. Different symbols for data points represent different runs.

For light of 4880 Å, which is just 5 meV below the exciton bound to the neutral donor (I_2) in CdS,[1] the denominator in the expression for α [see Eq. (2)] is near resonance, resulting in huge rotations. This is dramatically illustrated in Fig. 2(a) where the transmitted intensity is plotted versus H keeping the plane of the analyzer Polaroid fixed. The separation between successive peaks in I_T corresponds to 180° rotation and these points are plotted in Fig. 2(b). By measuring R versus T at 4880 Å, one finds that the

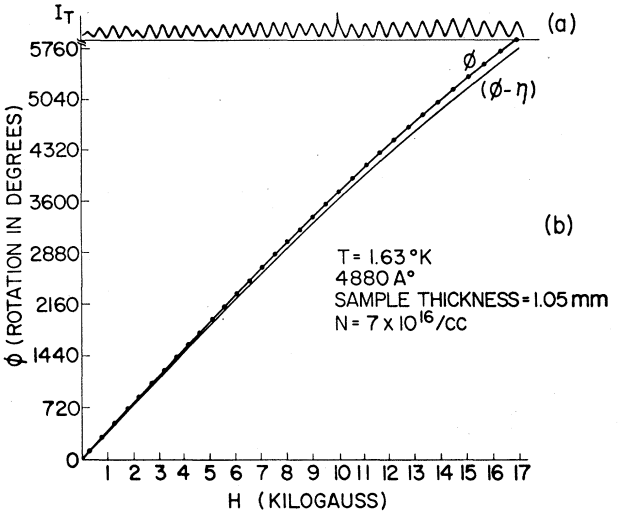

FIG. 2. (a) Transmitted intensity, I_T, versus H with fixed position of Polaroid analyzer. Separation between peaks corresponds to 180° of rotation. (b) Curve labeled φ is plot of peaks in (a) and $\varphi - \eta$ is spin FR.

crystal background $d\eta/dH = 8.6$ deg/kG mm, which, while a much smaller fraction of R than at 4965 Å, is still an observable correction to the spin FR. Again $\varphi - \eta$ versus H in Fig. 2(b) is found to follow the appropriate Brillouin function to a few percent.

In Table I are listed the measured values for the spin FR at three different wavelengths along with the cross section calculated from Eq. (7). Since CdS is not cubic, there is more than one cross section; i.e., it cannot be represented by one constant, α. The $d\sigma/d\Omega$ associated with the FR in our case is that for which the electric vectors of both the laser and the Raman light are perpendicular to the c axis with $\vec{H} \perp \vec{c}$.

In comparing the experimental results at 4880 Å with theory, it is adequate to consider only the I_2 exciton as done by Thomas and Hopfield.[1] However, for light of longer wavelengths it is necessary to consider the bound excitons from all three valence bands, especially the I_{2B}. The results of this more complete calculation are listed in the last column in Table I. The relatively small discrepancies between $(d\sigma/d\Omega)_{FR}$ and $(d\sigma/d\Omega)_{theor}$ could be easily accounted for by the small uncertainties in both the oscillator strength of the excitons and the appropriate energy denominators in Eq. (2). The orders-of-magnitude discrepancy between the experimental values of $d\sigma/d\Omega$ quoted in Refs. 1 and 2 is probably due to a very strong surface absorption which occurs for mechanically polished crystals used in Ref. 2 as compared to as-grown platelets used in Ref. 1. This emphasizes the desirability of measuring the SFRS cross section by FR.

Since $\varphi - \eta \sim \langle \sigma_z \rangle$, $R - a = d(\varphi - \eta)/dH$ is proportional to the donor spin susceptibility χ, so that the *near-resonant* FR provides a very sensitive as well as *selective* way of measuring magnetic properties of the donors. Other magnetic impurities such as Mn^{2+} which may dominate the bulk susceptibility of the sample contribute insignificantly to φ at 4880 Å. The utility of the FR in measuring interaction between donors is illustrated in Fig. 3 where $(R - a)^{-1}$ is plotted versus T. The data do not follow a Curie law but indicate the presence of antiferromagnetic exchange interactions. Their effective magnitude may be estimated roughly by extracting from a least-squares fit to the data a Curie-Weiss Θ of 0.3 ± 0.1 K. Herring and Flicker[6] have calculated the asymptotic behavior of the exchange between two hydrogen atoms. Applying Eq. (19) of their paper to the mean donor separation in our sample, $\langle r \rangle = 0.55 N^{-1/3} = 132$ Å, and using a rydberg of 30 meV[7] and a Bohr radius of 25 Å, we find $J/k = 1.9$ K. This comparison of J

TABLE I. Values of measured FR induced by bound donor-electron spins, and spin-flip cross sections as determined from FR, $(d\sigma/d\Omega)_{FR}$, Raman scattering, $(d\sigma/d\Omega)_{RS}$, and theoretical calculations. FR data are for sample containing 7×10^{16} In/cm^3 and for $T = 1.63$ K.

λ (Å)	Spin FR R (deg/kG mm)	$\left(\frac{d\sigma}{d\Omega}\right)_{FR}$ (cm^2)	$\left(\frac{d\sigma}{d\Omega}\right)_{RS}$ (cm^2)	$\left(\frac{d\sigma}{d\Omega}\right)_{theor}$ (cm^2)
4880	363	1.9×10^{-18}	4×10^{-18} [a]	4.4×10^{-19}
4965	8.8	9.9×10^{-22}	3×10^{-20} [a]	6.4×10^{-22}
5145	2 ± 1	4×10^{-23}	10^{-25} [b]	1.8×10^{-23}

[a] See Ref. 1. [b] See Ref. 2.

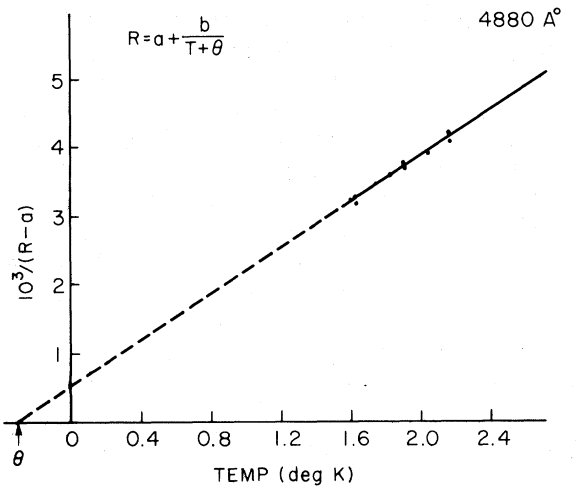

FIG. 3. Reciprocal of spin rotation, $1/(R-a)$, versus T showing extrapolated Curie-Weiss constant, $\Theta = 0.3 \pm 0.1$ K.

and Θ is intended to be order of magnitude only. As there is an extremely broad distribution of J values,[8] and as we do not have an exact solution for the susceptibility of an amorphous antiferromagnet, it is difficult to precisely relate the Θ observed in our range of T to the J distribution. Equally as interesting as attempts at such a fit would be experiments at still lower temperatures which could reveal features of ordering in an amorphous antiferromagnet.

Measurements have been taken on more concentrated samples ranging up to $N = 6\times10^{18}$. Beyond $N = 2\times10^{18}$ one finds only a temperature-independent FR which does not saturate with field characteristic of the Pauli susceptibility of a free-electron gas. By contrast, in the intermediate region just beyond the Mott transition ($N \sim 2\times10^{17}$) one finds both temperature-dependent as well as temperature-independent components to χ,[9] characteristic of a strongly correlated electron gas.[10] These results will be reported more fully elsewhere.

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[1]D. G. Thomas and J. J. Hopfield, Phys. Rev. 175, 1021 (1968).

[2]J. F. Scott, T. C. Damen, and P. A. Fleury, Phys. Rev. B 6, 3856 (1972).

[3]R. Romestain, S. Geschwind, G. E. Devlin, and P. A. Wolff, Phys. Rev. Lett. 33, 10 (1974).

[4]The connection between spin FR and SFRS was suggested by P. S. Pershan, J. P. van der Ziel, and L. D. Malmstrom, Phys. Rev. 143, 574 (1966), and by Y. R. Shen and N. Bloembergen, Phys. Rev. 143, 372 (1966), and first demonstrated experimentally for magnon Raman scattering in magnetically ordered materials by H. LeGall, J. P. Jamet, and B. Desormieres, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971). However, this explicit connection as expressed by our Eq. (7) and applied by us here has heretofore been overlooked for the simpler case of semiconductors.

[5]This FR, η, has been already studied in several II-VI compounds [see M. Balkanski and E. Amzallag, Phys. Status Solidi 30, 407 (1968), and references therein] but these experiments were usually performed at high temperature and too far from the I_2 line to see the spin FR.

[6]C. Herring and M. Flicker, Phys. Rev. 134, 362 (1964).

[7]S. Toyotomi and K. Morigaki, J. Phys. Soc. Jpn. 25, 807 (1968).

[8]P. R. Cullis and J. R. Marko, Phys. Rev. B 1, 632 (1970).

[9]J. D. Quirt and J. R. Marko, Phys. Rev. B 5, 716 (1972), and 7, 3842 (1973).

[10]W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 4302 (1970); K. A. Chao and K. F. Berggren, Phys. Rev. Lett. 34, 880 (1975).