Z is the atomic number, Z_0 is the inert-element atomic number that begins the period which includes the actual Z, and $(E_F)_Z$ is the corresponding Fermi energy.

The general-model pseudopotential presented enables simple computation of the form factors in the small-wave-number range which is an appreciable advantage, especially in the estimation of electronic properties.

[1]W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).
[2]L. J. Sham, Proc. Roy. Soc., London, Ser. A 283, 33 (1965).
[3]A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).
[4]V. Heine and I. Abarenkov, Phil. Mag. 9, 451 (1964).

Anomalous Double Spin-Flip Raman Scattering in CdS, and a Visible Spin-Flip Laser

J. F. Scott and T. C. Damen
Bell Laboratories, Holmdel, New Jersey 07733
(Received 16 December 1971; revised manuscript received 10 March 1972)

We have observed a peak in the inelastic light scattering of CdS in high magnetic fields at an energy slightly less than twice the bound electron spin-flip energy μgH. The intensity, selection rules, field dependence, and binding energy of this process cannot be explained as second-order scattering. At very high excitation energies (≥ 1 MW/cm^2) the single spin-flip scattering becomes stimulated, with a sharp threshold and high conversion efficiency.

We have examined the inelastic light-scattering spectra of CdS in high magnetic fields (40–100 kG) and have found, in addition to the $\Delta S = 1$ spin-flip scattering from bound[1] and free[2] electrons reported previously, a strong peak in the spectrum at an energy slightly (0.25 ± 0.05 cm^{-1}) less than twice the shift of the $\Delta S = 1$ bound electron energy μgH (7.85 cm^{-1} at 89 kG).[3] The intensity, selection rules, field dependence, and apparent binding energy of the double spin-flip process cannot be accounted for by model calculations which treat the $\Delta S = \pm 2$ scattering as second order; however, all these anomalies have been interpreted via a theory[4] based on a simple model of the electronic interactions.

Our experiments consist of Raman scattering from CdS specimens having carrier concentrations between $n = 1 \times 10^{16}$ and 5×10^{17} cm^{-3}. These were obtained from Eagle Picher and were shown by spectrochemical analysis to contain 10^{17}–10^{18} cm^{-3} In donor concentration. The samples were illuminated with light at 4765, 5880, 4965, and 5145 Å from a 2-W argon ion laser at temperatures between 2.0 and 25°K and in magnetic fields from 40 to 100 kG. At these low temperatures all samples exhibited spin-flip scattering ($\Delta S = \pm 1$) with selection rules compatible with those calculated by Thomas and Hopfield[1] for electrons bound to neutral donors having C_{3v} site symmetry. In particular, α_{XZ}, α_{XX}, and α_{XY} polarizability components were equally strong, where Z is the direction of applied field. In contrast, the same samples exhibited only $\alpha_{XZ} = \alpha_{YZ}$ scattering at higher temperatures (>80°K), as reported earlier by Fleury and Scott.[2] The low-temperature scattering intensity is attributed to bound-electron spin flip, whereas the high-temperature scattering is attributed to free electrons. In addition to selection-rule differences, the free- and bound-electron spin-flip processes exhibit different linewidths and different dependences upon momentum transfer or scattering angle.[5] The free- and bound-electron g values are very nearly the same, both lying between 1.80 and 1.86.

In the present study, we have observed, in addition to the $\Delta S = \pm 1$ spin-flip processes reported in Refs. (1) and (2), sharp lines at energies slightly less than twice the single spin-flip energy $\Delta = \mu gH$. These are shown in Fig. 1 for an $n = 1 \times 10^{16}$ cm^{-3} sample at 40 kG and 2.0°K. Significant features of the higher-energy feature are (1) its intensity is $(5 \pm 1)\%$ of that for the $\Delta S = 1$ line; (2) its selection rules are exactly the same as those for the $\Delta S = 1$ process, i.e., the relative intensity $I(\Delta S = 2)/I(\Delta S = 1)$ is independent of polarizability tensor component (5% for α_{XX}, α_{XY}, and α_{XZ}; $z \| \vec{H}$); (3) its frequency is given by $\omega = 2\Delta - (0.25 \pm 0.05$ cm$^{-1})$, where $\Delta = \mu gH = 3.52$ cm^{-1} at 40 kG. That is, the fea-

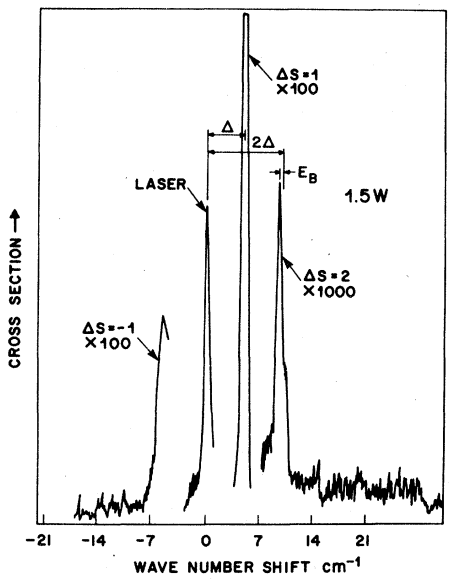

FIG. 1. Single and double spin-flip scattering in $n \cong 1\times10^{16}$-cm^{-3} CdS at 2.0°K and 40 kG. Note the changes in intensity scale for the features. The energy 2Δ is shown to make the 0.25-cm^{-1} shift of the double spin-flip line apparent. 4880-Å excitation at 400 mW and 20-μm slit width; right-angle scattering geometry.

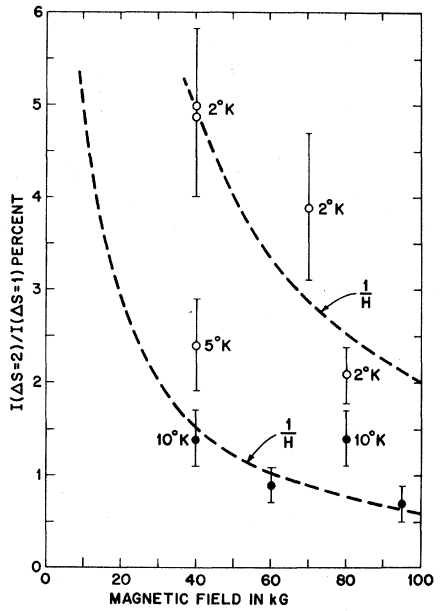

FIG. 2. Intensity ratio of double spin-flip scattering to single spin-flip scattering versus magnetic field for $n \cong 1\times10^{16}$-cm^{-3} sample at several temperatures. 4880-Å excitation; right-angle scattering geometry $\dot{X}(ZY)Z$ with $Y \| H$ and $Z \| [0001]$.

ture exhibits linearly field-dependent frequency with slope exactly $2\mu g/\hbar$, but does not extrapolate to $\omega = 0$ at zero field. We interpret this feature as a $\Delta S = \pm 2$ double spin-flip transition.

The temperature and field dependence of the $\Delta S = 2$ cross section relative to that for $\Delta S = 1$ is shown in Fig. 2. Note that for this specimen ($n \cong 1\times10^{16}$ cm^{-3}; Eagle Picher UHP) the intensity ratio is 0.8 – 1.5% at 10°K and approximately field independent, whereas at 2.0°K, a dependence of roughly $1/H$ is observed, with a measured ratio of (5 ± 1)% at 40 kG. Since the observed linewidths and selection rules are indicative of spin flip from impurity electrons (whose spin levels are dispersionless), the energy shift of the observed level from $2\mu gH$ can be assumed to be a direct measure of the attractive energy E_B of the two-electron spin state. This attractive energy could arise in two different ways. If the nearby impurity-bound electrons interact by exchange in the ground state, the interaction creates dispersion in an otherwise dispersionless spin level. The small shift E_B would be interpreted in this model as due to finite wave vector, with spin energies at q and $-q$ not adding up to twice the $q = 0$ value. Alternatively, the attractive energy could arise from exchange in the virtual excited state. In this case, the apparent shift E_B would represent a true binding energy of the two-electron state.

These two models predict different line shapes. Whereas the very narrow linewidth shown in Fig. 2 favors the excited-state exchange, the width does extend to $2\Delta = 2\mu gH$, which is compatible with the ground-state dispersion model. Further theoretical discussion is given in the accompanying paper by Economou, Ruvalds, and Ngai.[4]

Note that a more detailed line-shape measurement will allow us to distinguish between these two theories. Thus, we will be able to determine the degree of spin delocalization, i.e., the magnitude of ground-state exchange.

We note also that the accompanying theory makes some prediction regarding change in the intensity ratio $I(\Delta S = 2)/I(\Delta S = 1)$ with laser wavelength [see Eq. (1b) in Ref. 4]. This dependence has not been assessed in detail experimentally; however, we have been unable to observe spontaneous double spin-flip scattering at 4965 or 5145 Å (only at 4765 and 4880 Å), and believe that the ratio plotted in Fig. 2 decreases at wavelengths longer than the 4880 Å.

Finally, the CdS sample with strongest double spin-flip scattering (10^{18} In) also exhibits a weak scattering feature about 0.8 cm^{-1} less than 3

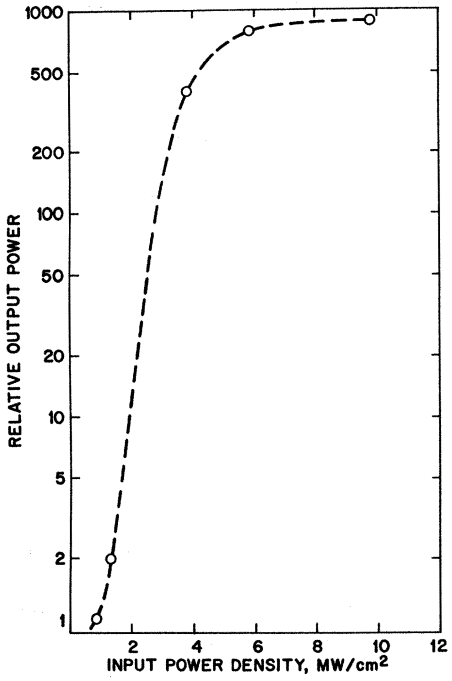

FIG. 3. Scattering cross section for single spin-flip scattering in 10^{18}-cm^{-3} In-doped CdS versus pump power. Forward scattering with propagation direction $\perp H$. 1 kW at 4925 Å focused to 100 μm diameter and attenuated by various calibrated neutral density filters. $T = 40$°K.

times the single spin-flip frequency μgH. The intensity ratios $I(1):I(2):I(3)$ are approximately 100:10:1, in accord with the accompanying theory.

We should mention that a completely different theory of double spin-flip scattering has been developed by Wolff.[6] Wolff's theory is based on near-field dipole radiation from one spin inducing spin-flip of a second nearby electron. This calculation provides cross sections of the right magnitude and predicts disappearance of the effect at high temperatures. It does not predict a binding energy E_B or any field dependence (Fig. 3). Hence these experimental details must be analyzed more carefully to allow us to determine which theory is correct.

At much higher pumping powers, we do observe stimulated scattering from the $\Delta S = \pm 1$ process. Figure 3 shows that at 40°K one sample exhibits a sharp threshold at about 4 MW/cm^2 for longitudinal pumping (forward scattering) at 4925 Å. The excitation consisted of a 3-kW dye laser operating at 0.3 Å linewidth, 500 nsec pulse length, and 5–10-Hz repetition rate. The conversion efficiency of this visible spin-flip laser was high, with 25–40% of the power output in the forward direction occurring at the spin-flip shifted frequency. [For the wavelengths used, the pump light (polarized $\perp C$) is attenuated much more than the spin-flip scattered light (polarized $\parallel C$), so that the actual conversion efficiency is much less than the 25% quoted above.]

We have thus produced a visible spin-flip laser analogous to the InSb infrared device of Patel and Shaw.[7]

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

[2]P. A. Fleury and J. F. Scott, Phys. Rev. B 3, 1979 (1971).

[3]J. F. Scott, P. A. Fleury, and T. C. Damen, to be published, and in Proceedings of the Quantum Electronics Conference, Montreal, May 1972 (to be published).

[4]E. N. Economou, J. Ruvalds, and K. L. Ngai, following Letter [Phys. Rev. Lett. 29, 110 (1972)]. A more detailed calculation by Y. Yafet is also in progress.

[5]J. F. Scott, T. C. Damen, and P. A. Fleury, to be published.

[6]P. A. Wolff, private communication.

[7]C. K. N. Patel and E. D. Shaw, Phys. Rev. Lett. 24, 51 (1970).