terials must encompass these transition metals. Unfortunately many experimental difficulties remain unresolved, and considerable effort needs to be expended in the development of techniques to produce a wider range of samples to permit systematic studies of the influence of the electronic configuration of the constituents on the properties of amorphous transition metals. Tunneling and Hall-effect measurements are definitely needed to complement the specific-heat and critical-field measurements available.

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Measurement of the Linear k Term in a Polar Crystal (CdS) by Spin-Flip Raman Scattering

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A large difference in widths and intensities between Stokes and anti-Stokes spin-flip Raman scattering lines of donor electrons in n-CdS has been observed. This asymmetry arises from the linear k term, $\lambda(\vec{k}\times\vec{c})\cdot\vec{s}$. In a diffusional linewidth, the term λ appears as $D(q\pm\lambda m^*/\hbar^2)^2$ from which we find $\lambda = 1.6\times10^{-10}$ eV cm in good agreement with our theoretical estimate. A new effect called Doppler *narrowing* is implied.

The energy of carriers in a *polar* crystal measured from the band minimum has, in addition to the usual term $\hbar^2k^2/2m^*$, a term[1] $\lambda(\vec{k}\times\vec{c})\cdot\vec{s}$ where $\vec{c}$ is a unit vector along the polar axis and s is the spin operator so that

$$E = \hbar^2k^2/2m^* + \lambda(\vec{k}\times\vec{c})\cdot\vec{s}. \tag{1}$$

This second term is analogous to a spin-orbit effect and is the interaction of the magnetic moment of the electron with the effective magnetic field which it sees as it moves in the polar field. Such terms linear in k have been proposed as a relaxation mechanism for conduction-electron spins in noncentrosymmetric crystal[2] and have been discussed and measured indirectly in collaborations by Hopfield, Thomas, and Mahan[3-5] for the valence band in CdS (which has the wurtzite structure), but have never been reported for a conduction band in any crystal.[6] We report here its first observation and direct measurement in a conduction band by spin-flip Raman scattering (SFRS).[7,8]

In SFRS, an electron in an external magnetic field $\vec{H}_0$, with a given spin orientation and $\vec{k}$ vector, is scattered to $\vec{k}+\vec{q}$ with a simultaneous spin flip, with $\vec{q}=\vec{q}_i-\vec{q}_s$ where $\vec{q}_i$ and $\vec{q}_s$ are the wave vectors of the incident and scattered light, respectively. The frequency shift of the light, $\Delta\nu = \Delta\omega/2\pi$, for $q \ll k$ is therefore given by

$$\Delta\omega = \frac{\hbar\vec{k}}{m^*}\cdot\left[\vec{q}\pm\frac{\lambda m^*}{\hbar^2}\left(\vec{c}\times\vec{h}_0\right)\right]+\frac{g\mu_B H_0}{\hbar}, \tag{2}$$

where $\vec{h}_0$ is a unit vector along $\vec{H}_0$ which determines the spin quantization direction[9] and the upper and lower signs ($\pm$) refer to the anti-Stokes and Stokes lines, respectively. Thus, the usual Doppler shift $\Delta\omega_D = (\hbar/m^*)\vec{k}\cdot\vec{q}$ is modified by the term containing λ. It is well known[8,10] that in the presence of rapid collisions, such that $(\hbar/m^*)\vec{k}\cdot\vec{q} \ll 1/\tau_c$, the Doppler shift is motionally narrowed and a diffusional linewidth Dq^2 is observed where $Dq^2 = [(\hbar/m^*)\vec{k}_F\cdot\vec{q}]_{Av}{}^2\tau_c = \frac{1}{3}v_F{}^2\tau_c q^2$ and the average is over all directions of $\vec{k}_F$. If one is therefore in a diffusional regime (which can usually be reached by making q small enough, i.e., near-forward scattering), the diffusional linewidth in a polar crystal is given by

$$\Delta\omega = D[\vec{q} \pm (\lambda m^*/\hbar^2)(\vec{c}\times\vec{h}_0)]^2, \tag{3}$$

where the upper and lower (±) signs refer, respectively, to anti-Stokes and Stokes. Note that the effect is maximum when $\vec{q}$, $\vec{c}$, and $\vec{h}_0$ are perpendicular to one another. Thus, λ can be directly determined from Eq. (3) from the measured difference between Stokes and anti-Stoles linewidths at a given $\vec{q}$ value.

In Fig. 1(a) is shown the SFRS spectrum taken with a Fabry-Perot interferometer scan for a sample of CdS toward the metallic side of the insulator-metal transition with carrier concentration of 7×10^{17} cm^{-3} at 1.8°K. The directions of $\vec{q}$, $\vec{c}$, and $\vec{H}_0$ are as shown with the scattering angle $\theta = 30°$ and the laser wavelength is 4880 Å. The difference in linewidths of the Stokes and anti-Stokes is readily apparent. In Fig. 1(b), only the direction of the magnetic field has been reversed while all other conditions remained the same, leading to a reversal in the widths of Stokes and anti-Stokes as predicted by Eq. (3). The same reversal in widths is also observed if the direction of $\vec{H}_0$ is kept the same but *the polar $\hat{c}$ axis is reversed*, as expected. The asymmetry vanishes with $\vec{H}\parallel\hat{c}$ and it has been verified in detail that it varies as $(\vec{q}\times\vec{c})\cdot\vec{h}_0$ for many different geometries. The linewidths observed were independent of H_0 and were studied in fields as low as a few hundred gauss.

Since the observed SFRS lines will have in addition to the diffusional component a nondiffusive part $\Delta\omega_0$ related to the lifetime broadening of the spin levels (T_1 and T_2 relaxation times), it is necessary to study $\Delta\omega$ at several values of $\vec{q}$ and especially to locate the minimum in $\Delta\omega$ vs $|q|$ to determine λ best. To optimize the asymmetry, a geometry in which $\vec{q}$ remained perpendicular to $\vec{c}$ as $|q|$ was varied was chosen and is shown in the inset of Fig. 2. The sample and mirror rotate together about an axis perpendicular to the figure. This arrangement has the additional feature that $2q_0\sin\frac{1}{2}\alpha = 2nq_0\sin\frac{1}{2}\theta = |q|$, where n is the index and q_0 the free-space wave vector of the laser light. Thus, $\Delta\omega = Dq_0{}^2(2\sin\alpha/2 \pm \lambda m^*/q_0\hbar^2)^2$ and the index does not enter. In Fig. 2 is plotted $(\Delta\nu_{\rm exp})^{1/2}$ vs $\sin(\alpha/2)$. It should be stated that the data are symmetric about the ordinate axis at $\alpha = 0$ with continuous slope on each branch. Indeed, data were taken at both $\pm\alpha$ and $\pm H_0$, with any sign change reversing the widths of Stokes and anti-Stokes lines. Thus, a narrow line may be plotted as anti-Stokes even though it was real-

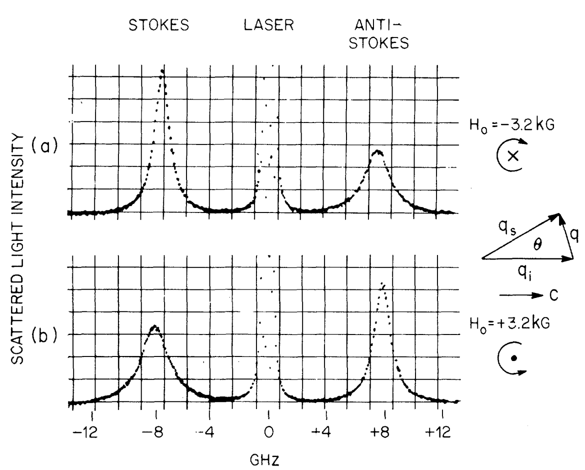

FIG. 1. (a) SFRS at internal scattering angle $\theta = 30°$ showing asymmetry in linewidths of Stokes and anti-Stokes due to the linear k term; (b) reversal of asymmetry with field reversal. The carrier concentration is 7×10^{17} cm^{-3}.

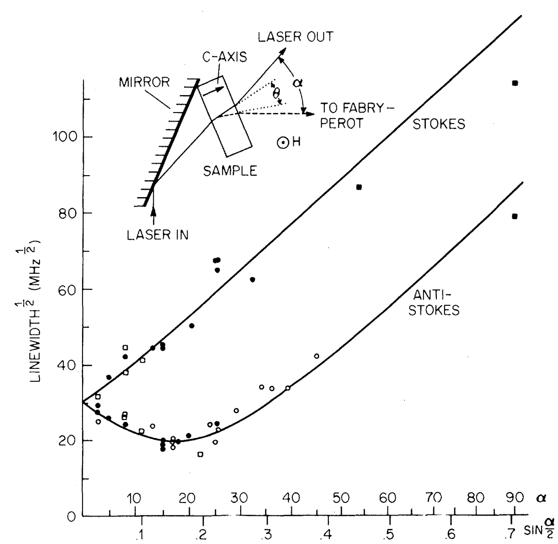

FIG. 2. SFRS linewidths in sample with a concentration of 1.8×10^{18} carriers/cm^3, showing asymmetry as a function of scattering angle and minimum at $\alpha = 18°$. Solid line is best fitted for low α, for two Lorentzian lines, $\Delta\nu_0$ and the diffusional line. See text.

ly, Stokes if it was taken with α or H_0 reversed from the chosen sign reference. Since $m^* = 0.2m$, the minimum at $\alpha = 18°$ (or $\theta = 6°$ since $n \sim 3$) according to Eq. (3) corresponds to a $\lambda = 1.6\times10^{-10}$ eV cm. This value of λ, to be further discussed below, corresponds to an equivalent magnetic field of 30 kG acting on the spin for $k_F = 3.6\times10^6$ cm^{-1}. In samples in which D varies with temperature, the same value of λ is observed at all temperatures and in samples with widely different D's whose values will be reported on later.

The minimum width $\Delta\nu_0 = 400$ MHz that is observed at $\alpha = 18°$ is presumably *narrower* than the EPR linewidth which should correspond to the width at $q = 0$, characteristic of the q in a microwave experiment. Thus by a choice of appropriate $\vec{q}$ in the optical experiment, one selects a Doppler shift which exactly cancels the effect of the linear k term. In an EPR experiment, the Doppler shift is negligible ($q \simeq 0$), so that the broadening effect of the linear $\vec{k}$ term for the electrons, even though collisionally narrowed, is still present. Thus, one has a remarkable situation in the SFRS that may be termed *Doppler narrowing* of a line.[11]

The solid lines in Fig. 2 are of the form $(\Delta\nu)^{1/2} = [\Delta\nu_0 + (4Dq_0^2/2\pi)(\sin\alpha/2 \pm \sin(18°/2)^2]^{1/2}$ with $\Delta\nu_0 = 400$ MHz and $(4Dk_0^2/2\pi) = 22.5$ GHz. These parameters were chosen to give the best fit to the data at low q values, since it is in this region that motional narrowing is most effective. At higher values of q, motional narrowing is less effective. The lines are then asymmetric with broad tails but have sharp peaks which are emphasized by the Fabry-Perot response. This distortion gives the appearance of a narrower line as seen in the data.

The term linear in k in the effective Hamiltonian arises from a third-order term in the energy of the form[4]

$$\lambda(\vec{s}\times\vec{k})\cdot\vec{c} = \sum_{\{|p\rangle\}} \frac{\langle s|(\hbar/m)\vec{k}\cdot\vec{p}|p\rangle\langle p|\zeta\vec{1}\cdot\vec{s}|p\rangle\langle p|eE\vec{c}\cdot\vec{r}|s\rangle}{E_g^2}, \tag{4}$$

where $|s\rangle$ refers to the conduction band and the sum is over the appropriate band p states; E_g is the band gap, E is the magnitude of the average odd electric field, ζ is the spin-orbit coupling or splitting in the p valence band. Calling by P the matrix element $\langle s|p_i|p\rangle$ and using $P = (mE_g/\hbar) \times\langle s|r_i|p\rangle$, one obtains

$$\lambda = P^2\frac{\hbar^2}{m^2}\frac{\zeta}{E_g^3}Ee = \frac{1}{2}\left(\frac{m}{m^*} - 1\right)\frac{\zeta\hbar^2}{mE_g^2}Ee, \tag{5}$$

since the effective mass m^* is given by $m/m^* - 1 = 2P^2/mE_g$. Using $m^* = 0.2m$, $E_g = 2.5$ eV, and $\zeta = 0.05$ eV and the value of λ derived from the value of $\vec{q}$ at $(\Delta\omega)_{\min}$ above, we find $E = 1.3\times10^9$ V/m. If one uses a crude point-charge model, neglecting polarization effects, treating the S^{2-} as having a charge of $2e$ and using a S-Cd distance of ~2.51 Å, a single S^{2-} ion will present a field of 4.6×10^{10} V/m at the Cd site. If the Cd-S tetrahedra were regular, the fields of the other three S^{2-} ions would of course cancel this field. Thus, a value of $E = 1.3\times10^9$ V/m would suggest just a 3% distortion of the tetrahedron which is consistent with what is known for the II-VI-compound wurtzite structures. It is interesting to compare our experimental value of $\lambda_c = 1.6\times10^{-10}$ eV cm for the conduction band in CdS with the value $\lambda_v = 0.5\times10^{-9}$ eV cm for the valence band derived by Mahan and Hopfield[3] from the reflectivity spectra of CdS.[4] This ratio is only 0.3 while one would expect it to be of order $\zeta/E_g = 0.02$. This discrepancy could be the result of the greater uncertainties attached to the interpretation of the reflectivity measurement or possibly some other as yet not understood factors.

Equation (1) applies to noninteracting electrons in the conduction band. Our experimental results show, nonetheless, that in different samples in the Mott-transition regime with widely different transport properties, i.e., different D values, that the value of α at $(\Delta\omega)_{\min}$ is still 18°, implying that the asymmetry is still given by the noninteracting mass m^*. Kane has shown[12] that for donor electrons forming an impurity band in the tight-binding approximation, and neglecting electron correlation, that indeed only a bare mass m^* enters in the λ term in Eq. (3). We suggest a generalization of this result along the following lines. Suppose that for electrons near the bottom of the conduction band one may write a many-body Hamiltonian $\mathcal{H}' = \sum_{i,j}(-\hbar^2\nabla_i^2/2m^* + V_{ij} + V_i)$, where m^* is the bare band effective mass derived in the $\vec{k}\cdot\vec{p}$ approximation, V_{ij} the electron-phonon, etc., interactions. $\mathcal{H}'$ will in general result in a diffusion constant, D, which will contain a renormalized mass $(m^*)^*$ whereas D in Eq. (3), as derived from Eq. (1), involves only m^*. Let ψ be an eigenstate of $\mathcal{H}'$. The addition of a term $\sum_i\lambda|(i\nabla_i\times\vec{c})\cdot\vec{s}_i$ to $\mathcal{H}'$ simply has the effect (apart from a constant energy shift) of multiplying ψ by a phase factor $\exp[i\sum_i(\lambda m^*/\hbar^2)(\vec{c}\times\vec{s}_i)\cdot\vec{r}_i]$. SFRS involves a transition matrix element of the type $\int\psi_f^* \exp(i\vec{q}\cdot\vec{r})\psi_i$, where a single spin is flipped in going from ψ_i to ψ_f. Hence the addition of the linear k term modifies this to $\int\psi_f^* \exp\{i[(\vec{q}\pm(\lambda m^*/\hbar^2)(\vec{c}\times\vec{h}_0)]\cdot\vec{r}\}\psi_i$, where $\vec{h}_0$ is discussed in Ref. 9 and the ± refer to opposite directions of spin flip. Thus $\vec{q}\to\vec{q}\pm(\lambda m^*/\hbar^2)(\vec{c}\times\vec{h}_0)$ and while in general $(m^*)^*$ may appear in D, it is m^* which appears in the λ term associated with $\vec{q}$ which describes the shift in momentum space.[13] While the validity of a number of assumptions related to the application of the $\vec{k}\cdot\vec{p}$ approximation in the presence of interactions needs more precise theoretical statement, the constancy of our q shift in widely different samples suggests its generality in line with the argument outlined above.

Another interesting consequence of the linear k term is that detailed balance operates in such a way that the ratio of the integrated intensities of Stokes to anti-Stokes in a fixed experiment is *not* equal to the Boltzmann factor. For a *given* scattering geometry, the difference between Stokes and anti-Stokes is that in one case an excitation $+\vec{q}$ is created whereas for the latter an excitation $-\vec{q}$ is destroyed. Under normal circumstances excitations $+\vec{q}$ and $-\vec{q}$ correspond to the same energy, whereas in the presence of the linear k term they do not so that one does not observe a Boltzmann-factor ratio. However, the $+\vec{q}$ excitation for $+\vec{H}_0$ has the same energy as $-\vec{q}$ in $-\vec{H}_0$. Thus, the Boltzmann-factor ratio holds for the Stokes of $+\vec{H}_0$ relative to the anti-Stokes of $-\vec{H}_0$ or the Stokes of $-\vec{H}_0$ relative to the anti-Stokes of $+\vec{H}_0$.

The linear k term also results in unequal integrated intensities of Stokes plus anti-Stokes for $\pm H_0$. This is quite clearly seen even when the differences in linewidths are not so apparent as is the case for larger q values. Further detailed calculations of these effects will be presented elsewhere.

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