direction of magnetization and the symmetry axis (the [001] axis for the array of Fig. 2). With a maximum concentration of 0.5 ions per atom, the above result gives a uniaxial anisotropy constant $K_1 \cong 10^5$ erg cm^{-3}, which is the correct magnitude.[12] The fact that Fe exhibits cubic anisotropy presents no difficulty, assuming that the JT centers can relax to tetrahedral sites defined by the cubic axis closest to the direction of magnetization. (The JT sites shown in Fig. 2 are z-type sites; there are equivalent x and y types.) Finally, we note that in fcc and hcp structures, the tetrahedral site cymmetry axis is along $\langle 111\rangle$ and hexagonal directions—the directions of easy magnetization for Ni and Co, respectively.[12]

The present model is essentially a Heisenberg description, with magnetic moments localized in the Anderson sense,[5] not on individual atoms but on tetratomic "molecules". Band electrons not directly affected by the JT coupling respond ferromagnetically to the polarizing field of the local moments, enhancing the latter. The most unusual feature of the present model is the primary role assigned to electron-phonon coupling in creating the magnetic state. If this idea is essentially correct, there exists the intriguing possibility that superconductivity and magnetism in transition metals share a common origin. At a more basic level, the ideas presented here imply that the constraint of translational symmetry for transition metals and their compounds may be overly severe and should be carefully considered.

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Optical Studies of Excess Carrier Recombination in *a*-Si:H: Evidence for Dispersive Diffusion

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Relaxation of photoinduced optical absorption following pulsed laser excitation was measured between 0.5 μs and 10 ms in doped and undoped a-Si:H as a function of temperature. The recombination was found to be bimolecular diffusion limited. The diffusion coefficient of the excess carriers is time dependent ($\sim t^{-0.3}$) in agreement with the drift mobility of photocarriers and the predictions of the continuous-time random-walk theory of dispersive transport in disordered materials.

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Photoinduced midgap ir absorption (PA) was recently observed[1-3] under steady illumination in amorphous (a-) semiconductors with tetrahedral bonding. We have studied the recombination of excess carriers by measuring relaxation of PA in doped and undoped a-Si:H following excitation by a short laser pulse. The decay is shown to be governed by diffusion-limited bimolecular kinetics with a *time-dependent* rate coefficient $b = b(t)$, which implies that the photocarriers' diffusion coefficient D is also a time-dependent quantity. The time dependence of D is a consequence of the dispersive nature of the transport in amorphous materials which has been theoretically[4,5] and experimentally[6] studied in relation to time-of-flight mobility experiments. This is the first time that non-Gaussian transport has been demonstrated in the purely diffusive motion of injected electrons during their recombination. A comparison with time-of-flight measurements indicates that in dispersive transport the time-dependent diffusion coefficient is proportional to the drift mobility at all times.

The PA decay was studied in undoped sputtered a-SI:H (8×10^{-4} Torr H_2), in B- and P-doped films deposited by glow discharge (GD) with 10^3 ppm (volume) of the dopant gas, and Gd a-$Si_{0.13}$-$Ge_{0.87}$:H. The PA was excited by pulses from a cavity-dumped rhodamine 6G dye laser with the following parameters: photon energy 2.1 eV, duration 200 ns, energy 60 nJ, and repetition rate 100 Hz. Each pulse produced an estimated average carrier density of 10^{16} cm^{-3}. The transient absorption was measured by monitoring the modulated transmission of a probe beam from a filtered tungsten lamp focused within the laser illuminated spot on the sample. The detection system consisted of a Ge photodiode (Judson J-16LD), and boxcar integrator (PARC 162) with 300-ns time resolution. The spectral range of the probe was from 0.6 to 1.4 eV which includes almost the full width of the PA band in a-Si:H.[1,2]

In Fig. 1, the induced absorption is plotted versus the delay time after the laser pulse, on logarithmic scales, for several temperatures from 80 to 306 K. The ordinate is the fractional transmission change $-\Delta T/T$ which is proportional to the number of PA centers N. A constant gate aperture of 0.5 μs was maintained at all delays so that no vertical adjustment of the data in any time range was required. Figure 1(a) shows the results for a-Si:H, Fig. 1(b) for a-Si:H heavily doped with phosphorus. Note that the time dependence of PA asymptotically approaches a power law weaker than t^{-1}. The decay is faster at higher temperatures but the temperature variation of the decay rate is weaker in the doped sample. Similar results were found in the B-doped a-Si:H and the Si-Ge alloy.

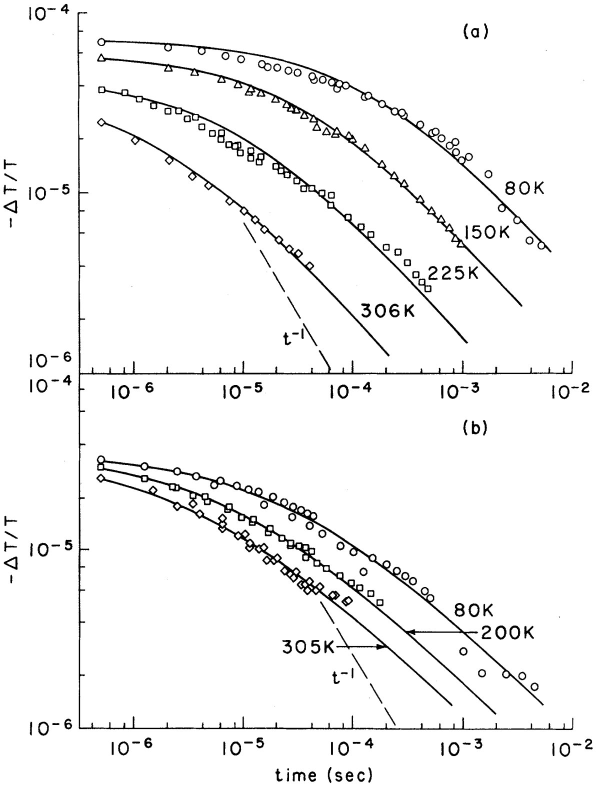

FIG. 1. Decay of photoinduced absorption following pulsed laser excitation in (a) undoped and (b) phosphorus-doped a-Si:H, as a function of temperature. Solid lines calculated from Eq. (5) with $\alpha = 0.7$ and 0.6, respectively. Broken lines show t^{-1} decay for comparison.

Steady-state PA measurements indicate that recombination of the PA centers is bimolecular.[1-3] If we assume that the initial carrier density is proportional to the intensity of the exciting laser light [$N_0(x) = N_0 \exp(-\alpha_l x)$, where x is measured from the surface and α_l is the absorption coefficient of the laser light], the bimolecular rate equation

$$dN/dt = -bN^2 \tag{1}$$

must be integrated over t and x. This gives for the time dependence of PA

$$-\frac{\Delta T}{T}(t) = \frac{\sigma}{\alpha_l b t}\ln\left(\frac{1 + bN_0 t}{1 + bN_0 t \exp(-\alpha_l d)}\right), \tag{2}$$

where σ is the absorption cross section of a PA center and d is the sample thickness.

Equation (1) predicts a t^{-1} decay at long times which is not observed (Fig. 1). We could explain the weaker time dependence by taking the coefficient b as a decreasing function of time. The physical basis for this approach is provided by the continuous-time random-walk (CTRW) theory of dispersive carrier transport in disordered solids.[4,5]

This theory describes the behavior of carriers moving among a random array of sites where the underlying event times, such as hopping or trapping times, are broadly distributed because of the disorder. The usual application is for the case of carrier motion in a biasing electric field in time-of-flight drift-mobility experiments.[4] In a wide variety of amorphous materials the results closely confirm the major features of the theory.[6] The transiting carrier packet obeys non-Gaussian statistics and the centroid of the carrier distribution has a time-dependent velocity $\sim 1/t^{1-\alpha}$. The dispersion parameter α depends on the microscopic properties of the material and may also be temperature dependent.[6]

We will now apply this theory to recombination kinetics in these materials. In particular, we consider the case of diffusion-limited bimolecular processes. The rate coefficient b defined in Eq. (1) can be written as[7]

$$b = 4\pi r_0 D, \tag{3}$$

where r_0 is the radius of the recombination sphere and D is the diffusion coefficient of the more mobile of the two reacting species.

We assumed that b has the form

$$b = B/t^{1-\alpha}. \tag{4}$$

This is the expected form for $b(t)$ since from theoretical considerations[8] $D(t) \sim 1/t^{1-\alpha}$ in dispersive materials. We will show that the experimental results are in agreement with Eq. (4). Integrating Eq. (1) with b from Eq. (4) gives for the PA decay

$$-\frac{\Delta T}{T}(\tau) = \frac{\sigma N_0}{\alpha_l \tau^\alpha} \ln\left(\frac{1+\tau^\alpha}{1+\tau^\alpha \exp(-\alpha_l d)}\right), \tag{5}$$

where $\tau = (BN_0/\alpha)^{1/\alpha} t$ is a normalized time.

The solid curves in Fig. 1 are fitted to the above equation with[1] $\sigma = 10^{-16}$ cm^2 and α_l taken from literature including a temperature correction.[9] The dispersion parameters α were taken from the results of drift-mobility experiments to be 0.7 and 0.6, independent of temperature, in undoped[10] and P-doped a-Si:H,[11] respectively. The agreement with the experimental data is remarkably good. Similar good fits were obtained in B-doped a-Si:H, which closely resembles the curves of Fig. 1(a), and a sample of a-Si$_{0.17}$Ge$_{0.83}$:H, where the decay was found to be almost two orders of magnitude faster.

The dependence of $\Delta T/T$ vs τ on excitation intensity predicted by Eq. (5) was directly verified by experiment.

The initial value of $|\Delta T|/T$ observed at 0.5 μs in the undoped sample is about three times smaller at 306 K than at 80 K [Fig. 1(a)]. We attribute this to recombination during the first 0.5 μs which is not resolved in our experiment, rather than to a variation of the quantum efficiency with temperature. [Compare Fig. 1(b) where this effect is smaller—consistent with the weaker variation of the decay rate with temperature.]

To characterize the decay we define an average rate coefficient $\bar{b} = B/\alpha t_0^{1-\alpha}$, where t_0 is the time required for $|\Delta T|/T$ to decay to 10% of its value at 0.5 μs. This somewhat arbitrary definition is necessary because the time average of $b(t)$ over an infinite interval vanishes. Our use of this lifetime t_0 parallels the definition of the transit time in dispersive drift-mobility experiments[6,11] and is similarly used as a rough measure of the duration of the experiment; the following results do not depend on the exact definition of t_0.

In Fig. 2 the logarithms of t_0 and $\bar{b}$ are plotted versus reciprocal temperature, along with the rate coefficient b of the undoped Si:H derived from steady-state PA measurements. Below about 80 K these quantities saturate; at high temperatures an activation energy can be defined.

The lifetime t_0 in a-Si:H and the photoconductivity (PC) transient lifetime reported by Fuhs, Milleville, and Stuke[10] have the same high-temperature activation energy (~ 80 MeV) and their magnitudes agree within a factor of 2. The aver-

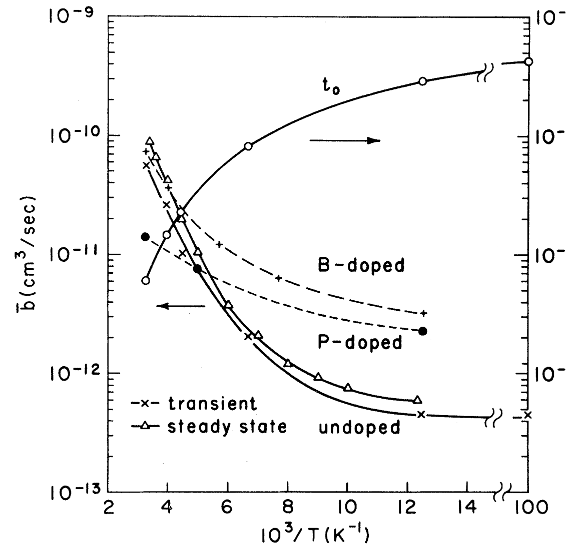

FIG. 2. Temperature dependence of the average recombination rate coefficient $\bar{b}$ derived from the decay measurements for boron-doped, phosphorus-doped, and undoped a-Si:H (left scale). Triangles are values of b from steady-state measurements on the undoped sample. The PA lifetime t_0 for undoped a-Si:H is also shown (right scale).

age rate coefficient $\bar{b}$ in a-Si:H is seen to agree well with the values obtained for b from steady-state measurements, both in magnitude and activation energy (120 meV). Also evident from Fig. 2 are the weaker temperature dependences of $\bar{b}$ in B- and P-doped samples, again in good agreement with steady-state PA measurements (not shown in this figure). With our assumptions the time-averaged mean mobility μ is proportional to $\bar{b}/T$ and therefore their activation energies should have comparable values, as is indeed the case. In a-Si:H for electrons the activation energies of μ determined from time-of-flight[12] and transient PC measurements[10] are in the range 130 to 160 meV; they are smaller in doped samples.[11]

If we assume the strict validity of the Einstein relation, a magnitude of the electron mobility can be calculated from our data by use of Eq. (3) and $\mu = e\bar{b}/4\pi r_0 kT$. Assuming that r_0 is in the range of 5–40 Å we obtain room-temperature mobilities of $(0.5-4)\times 10^{-3}$, $(0.5-4)\times 10^{-3}$, $(1-8) \times 10^{-4}$ cm^2/V·s in undoped and B- and P-doped samples, respectively. These values are in the range of reported drift mobilities.[10-12]

The insensitivity of the PA lifetime t_0 to doping ($t_0 \simeq 60$, 60, and 200 μs for Si, Si:B and Si:P, respectively) supports the conclusion from the photoconductivity work[13] that when the kinetics are bimolecular (high illumination levels) the recombination does not depend on Fermi-level position as with monomolecular kinetics (low illumination).

The temperature-independent α in all samples indicates hopping transport[6, 10] which is consistent with the earlier identification of PA transitions involving localized states.[1] Therefore the activation energy of the mobility is the barrier for direct hopping and not an energy for thermal detrapping. It is, however, surprising that the same value of α also fits the data in the low-temperature regime where the mobility saturates.

We propose that the dispersive mobility found to influence the PA decay in this work should be considered also in other types of transient experiments which have diffusion-limited kinetics, bimolecular as well as monomolecular. An important example is the photoluminescence (PL) decay in amorphous silicon which was found[14] to be dominated by nonradiative recombination up to 50 ns. If we assume a diffusion-limited monomolecular process with a time-dependent diffusion coefficient $D \sim 1/t^{1-\alpha}$ this yields a PL intensity which decays as $\exp(-t/\tau)^{\alpha}$ and improves the fit to the published short-time PL decay data in a-Si:H.

The decay of the photoinduced midgap absorption band in a-As$_2$Se$_3$ in the range from 10^{-8} to 10^{-2} s was recently reported.[15, 16]. When the initial photoinduced carrier density exceeded $\simeq 10^{18}$ cm^{-3}, an asymptotic power-law decay weaker than t^{-1} was observed,[15] indicating non-Gaussian diffusion-controlled recombination. However, a change to t^{-1} behavior at low densities ($N \leq 10^{16}$ cm^{-3}) was also seen,[16] the origin of which was not discussed.

In conclusion, the decay of photoinduced absorption has shown that bimolecular in a-Si:H is governed by a dispersive diffusion mechanism described by the CTRW theory. The agreement between the transport parameters found by this method with those observed by time-of-flight measurements indicates that the assumption of the validity of the Einstein relation for dispersive transport is plausible. We propose that dispersive transport may play a role in recombination processes seen in other experiments as well.

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X-Ray Absorption Study of Mixed-Valence TmSe

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The L_{III} x-ray absorption edge of Tm in TmSe yields a temperature-independent valence of 2.58± 0.07. The thermal damping of the extended x-ray absorption fine structure of TmSe is nearly identical to that of ErSe. This indicates very weak coupling of breathing shell charge fluctuations of the Tm ions to the phonons and very little static disorder of the lattice.

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In this Letter we wish to report on L_{III} x-ray absorption spectra of mixed-valence TmSe and several integral-valence reference compounds. The study was undertaken to test the potential of x-ray synchroton radiation for mixed-valence research in general and to address two controversial aspects of the physics of TmSe in particular. X-ray absorption should be a powerful tool in mixed-valence research for two reasons: First, one can measure the ratio of both configurations (the valence) through the structure of the spectrum within a few electronvolts around the absorption edge.[1] Second, one can obtain the instantaneous distribution of radial distances to the neighbors of the unstable $4f$ ions, averaged over the sample, from an analysis of the extended x-ray absorption fine structure (EXAFS). This distribution gives, e.g., information about microscopic dynamic disorder of the lattice due to coupling of valence fluctuations to phonons. Both measurements can be done over a wide range of temperatures, pressures, and concentrations.

Although TmSe is probably the most extensively studied mixed-valence compound,[2] there is still controversy over the fractional valence, and, more importantly, it is uncertain whether the ground-state configurational mixture is dynamic or static. In well-characterized stoichiometric samples the valence is near 2.75, if deduced from the lattice constant at room temperature,[2] or near 2.55, when deduced from the Curie constant or from the magnetic neutron cross section above 70 K.[3] The dynamic nature of the low-temperature mixture is inferred from circumstantial evidence[2] but cannot be verified directly by Mössbauer isomer shift, which is very small for Tm and overshadowed by large hyperfine splittings.

The magnetic fluctuations, while being fast and temperature independent above 70 K, slow down linearly with decreasing temperature below 70 K and eventually are slow enough to admit magnetic order below 3 K,[4] which is in the range of magnetic ordering temperatures for normal, stable-valence Tm compounds (e.g., TmS). The low-temperature resistivity of stochiometric samples points to an insulating ground state.[5] Thus, while there is circumstantial evidence to the contrary,[2] there are also strong arguments for a static valence mixture in TmSe at $T \rightarrow 0$ K.

The uncertainties about the ground state of TmSe illustrate the need for experimental evidence of configurational motion of mixed-valence materials which goes beyond the magnetic fluc-