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Magneto-optical properties of the DX centre in $Al_{0.35}Ga_{0.65}As$:Te

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Abstract. Magneto-optical absorption spectra of a 0.4 mm thick, single-crystal $Al_{0.35}Ga_{0.65}As$:Te sample give evidence for two bleachable absorbers, one of which is identified as the DX centre. The bleached-state absorption coefficient and magnetic circular dichroism (MCD), measured from 0.66 to 2.2 μm at 1.7 K, are adequately described by the Drude free-electron model, in terms of which a value for the electron effective mass is obtained. Cooling the sample in darkness leads to transmission transients, from which the absorption coefficient and optical-conversion cross section for the bleachable deep DX ground state are derived. The MCD at the beginning of each transient is identified also with the DX ground state, and its temperature dependence reveals that the bulk of it has a non-paramagnetic origin. We conclude that the paramagnetic contribution to the MCD from the DX ground state is very small, being less than 0.004 % of its peak absorption coefficient. This provides strong support to the diamagnetic ground-state, negative-U model of Chadi and Chang. The origin of the second bleachable absorber (threshold $\sim$1.6 eV) has not been established.

1. Introduction

Large lattice relaxations affect the electrical and optical properties of defects in many solids. Such effects are intuitively expected for ionic solids, where Coulombic forces induce large atomic displacements after a change in electronic charge distribution. Examples are F centres in alkali halides [1] and indium impurities in CdF_2 [2].

Large lattice relaxations are also found in the more-nearly covalent, compound semiconductors and even in perfectly covalent, elemental semiconductors. Prototypical examples are the vacancy [3] in Si and the DX centre in AlGaAs and other compound-semiconductor alloys [4, 5]. The recent focus on DX stems in part from its influence on AlGaAs/GaAs modulation-doped field-effect transistors, which are being developed for high-speed circuit applications. More fundamentally, the DX phenomenon is a fascinating, challenging and still unsolved, scientific puzzle.

It is now well established that DX centres in $Al_xGa_{1-x}As$ arise from the isolated dopants which control n-type conductivity [4]. For $x > 0.22$, these group IV or group VI impurities induce both a deep level and a shallow effective-mass level in the gap. The deep level's optical ionization energy is very much larger than its thermal one. The shallow level can be metastably occupied below 100 K, resulting in persistent conductivity. Recapture by the deep level is a thermally activated, multiphonon process; optical capture does not occur. Large lattice relaxation accounts for these features, though its extent and microscopic nature are still in question.

Chadi and Chang [6, 7] have predicted that group VI donors become deep when an adjacent group III host atom breaks away in a $\langle 111 \rangle$ direction from the donor, and this distortion is only stable if the defect binds two electrons. Hence, the DX centre should be a negative-U system [8], and diamagnetism is expected for the deep negatively charged state since the two spins should pair oppositely.

Prominent among the many experiments performed to test the DX for negative-U properties have been attempts therefore to determine the magnetic state of the deep level. Conflicting static magnetic susceptibility measurements have been reported, one concluding that the ground state is paramagnetic [9], another concluding that the observed paramagnetism is an order of magnitude smaller than predicted assuming equal free spin and DX concentrations [10]. The failure [11, 12] to observe spin resonance associated with the deep level is consistent with negative U, but there are many possible reasons for failure to detect a paramagnetic defect (inhomogeneous alloy broadening, rapid spin-lattice relaxa-

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tion broadening, etc), and this also must be considered inconclusive.

Our purpose in the present work is to determine the paramagnetic contribution to magnetic circular dichroism (MCD) in the near-infrared absorption band of the deep DX state. This contribution is relatively insensitive to the width and relaxation times of the ground Zeeman-split states and should therefore more nearly reflect the ground state static susceptibility. In addition, being detected in an absorption band specific to the DX centre, the measurement is defect specific. Therefore, if a paramagnetic component is detected, it will convincingly rule out negative-U properties of DX. On the other hand, if none is detected, it will represent a strong argument for DX negative-U properties.

2. Experiment and results

MCD arises from spin–orbit interaction in the excited state involved in the optical absorption transition [13]. Its magnitude should therefore reflect the atomic spin–orbit interaction of the constituent atoms in the core of the defect. For this reason, the heavier atom tellurium was selected as the DX donor in our studies.

Our 0.037 cm thick, LPE, $Al_{0.35}Ga_{0.65}As$:Te sample had its substrate lapped off prior to measurements. Sample transmittance and MCD were measured at liquid-helium temperatures in an optical-access, superconducting magnet cryostat.

When AlGaAs is cooled in the dark, some DX centres may remain in the metastable shallow state, in principle. Hence, we must first characterize the magneto-optical properties of the metastable state in order to correctly identify those effects arising exclusively from the ground state. For this purpose, the optical-absorption coefficient, α_m, was measured after white-light illumination converted all of the DX centres to their metastable states. Figure 1 presents α_m versus wavelength λ. Fundamental absorption is dominant for $\lambda < 0.65\ \mu m$. The long-wavelength dependence is approximately λ^2 as predicted by the free-electron, Drude model, which gives [14, 15]

$$\alpha_m = \frac{Ne^2}{m^* nc^3 \pi \tau_e} \lambda^2 \tag{1}$$

where c is the speed of light, n the index of refraction of the material, e the electron charge, τ_e the relaxation time, m^* the effective mass and N the free-carrier concentration. The best fit of the function $\alpha = (\text{const})\ \lambda^2$ to the data is the smooth curve in figure 1.

Magnetic circular dichroism (MCD) is defined as $\alpha_L - \alpha_R$, where α_L (α_R) is the absorption coefficient for left (right) circularly polarized light propagating along the magnetic field direction. Figure 2 presents the measured MCD versus magnetic field at 0.8 and 1.4 μm after white-light bleaching. A spectrum without the sample shows that the instrumental background circular dichroism is field independent, and we take this as our zero, as shown. The MCD is positive, linear in magnetic field B and increases with wavelength. Measurements at $T = 1.7$ K and 4.2 K give identical results within experimental uncertainty, showing that paramagnetism of the metastable state plays an insignificant role in its MCD.

Figure 3 plots the slopes of the metastable state MCD versus wavelength from 0.9 to 2.0 μm. The data increase approximately as wavelength cubed, as indicated by the best cubic fit curve. The theory of the Faraday effect [16], using the Drude conductivity tensor, gives the expression

$$\text{MCD} = \frac{16\pi\sigma_0\omega_c}{nc\tau_c^2\omega^3} \tag{2}$$

where $\omega_c = eB/m^*c$ is the cyclotron frequency and $\sigma_0 = Ne^2\tau_e/m^*$ is the DC conductivity. Equation (2) is positive, linear in B and cubic in λ, in agreement with our observations.

Dividing equation (2) by equation (1) gives the simple relation

$$\frac{\text{MCD}}{\alpha_m} = 4\frac{\omega_c}{\omega}. \tag{3}$$

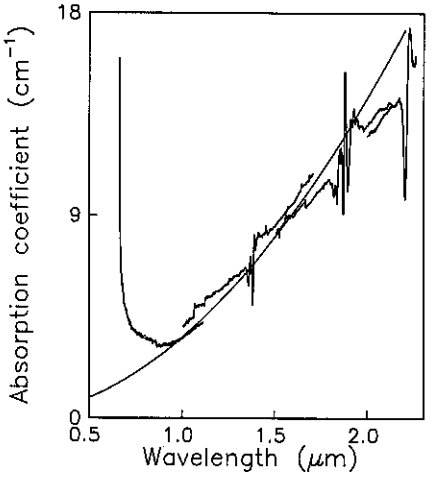

Figure 1. Absorption spectrum of $Al_{0.35}Ga_{0.65}As$:Te at 1.7 K after white-light illumination.

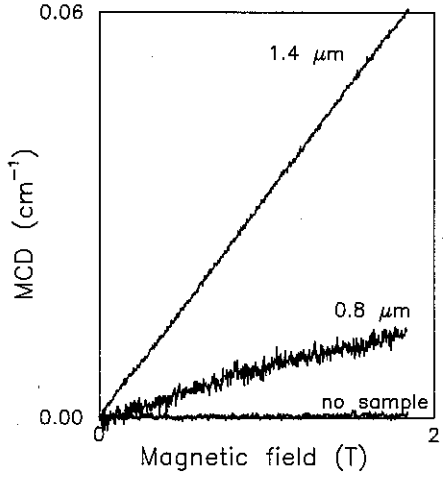

Figure 2. Field dependence of 1.7 K, $Al_{0.35}Ga_{0.65}As$:Te MCD after white-light illumination.

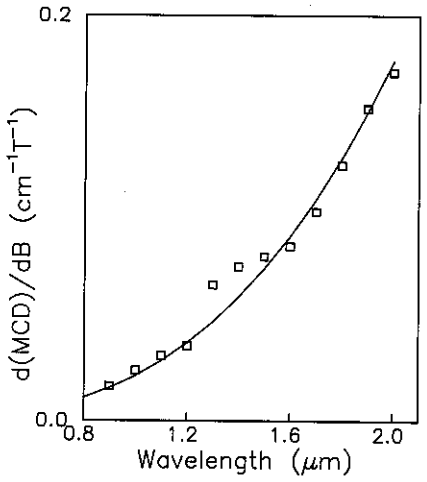

Figure 3. Spectral dependence of 1.7 K, $Al_{0.35}Ga_{0.65}As$:Te MCD after white-light illumination.

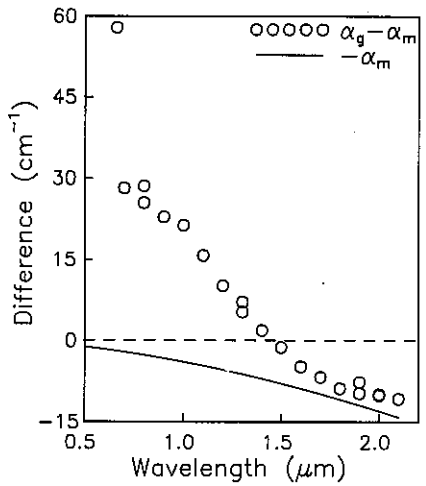

Figure 5. Spectral dependence of $\alpha_g - \alpha_m$. The smooth curve represents $-\alpha_m$ from Figure 1.

Equation (3) together with our data gives $m^* = 0.06\, m_0$, which compares well with the value $0.08\, m_0$ predicted [17] and measured [18] for the Γ minimum when $x = 0.35$. Evidently, the Drude model adequately describes both free-carrier absorption and MCD.

The optical transmission is strongly time dependent after cooling the sample in the dark. Figure 4 presents the transmitted intensity versus time at wavelengths 0.7 μm and 1.6 μm. At time $t = 0$ the shutter is opened, and the 0.7 μm transmission increases from I_0 to a value I_∞ as absorption is bleached. At time 1.6 μm, transmission decreases exponentially to a saturation value I'_∞. Additional white-light illumination further reduces the transmission to its final value (I_∞). The 1.6 μm $I'_\infty(I_\infty)$ levels persist unchanged in darkness for 30 min after terminating the 1.6 μm, or additional white-light, illumination. The significance of these two transient effects will be returned to later.

If bleachable absorbers, initially in their ground states, are completely converted to the metastable (free-carrier) state, then the difference between ground- and metastable-state absorption coefficients is

$$\alpha_g - \alpha_m = -\frac{1}{d}\ln\left(\frac{I_0}{I_\infty}\right). \tag{4}$$

Figure 5 presents $\alpha_g - \alpha_m$ (open circles) versus λ. For $\lambda \gtrsim 1.5$ μm, $\alpha_m > \alpha_g$, and the data approach the negative of the $\alpha_m \sim \lambda^2$ behaviour of figure 1, revealing that α_g is negligible here.

The open circles of figure 6 are estimates of α_g obtained by adding values of α_m (scaled by a factor of 0.75) determined from the smooth curve of figure 1 to the $\alpha_g - \alpha_m$ data of figure 5. (The data of figure 5, determined from equation (4), required no change of the optical set-up and are therefore relatively accurate and reproducible. On the other hand, the scale of the results in figure 1 depends on our estimate of the incident intensity, I_i. This is determined by lifting the sample, which can perturb the delicate optical alignment. The 0.75 scaling factor required to match the long-wavelength tail in figure 5 is

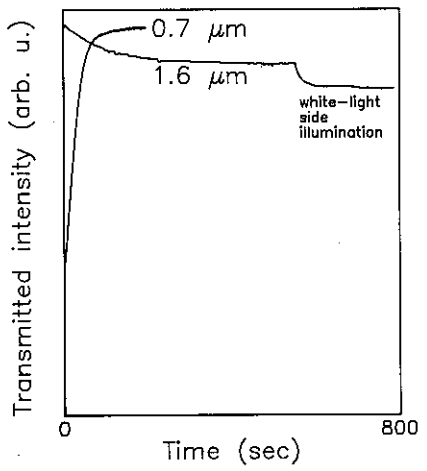

Figure 4. Transmission transients observed after cooling $Al_{0.35}Ga_{0.65}As$:Te to 1.7 K in the dark. The effect of white-light side illumination on the long-wavelength transient is also shown.

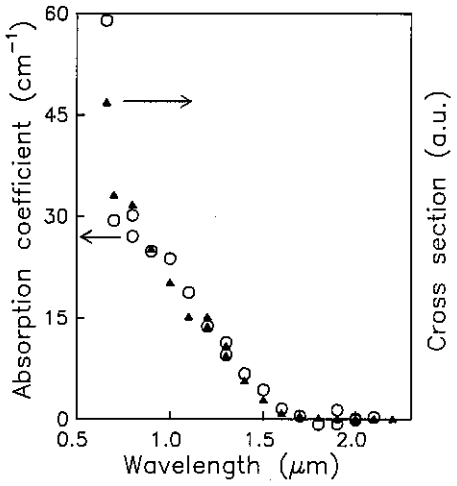

Figure 6. Spectral dependence of ground state absorption coefficient (open circles) and conversion cross section (full triangles) for bleachable absorbers in $Al_{0.35}Ga_{0.65}As$:Te at 1.7 K.

fully consistent with our estimate of the accuracy of the absolute scale for the data of figure 1.) The α_g values are seen to rise to a 30 cm^{-1} plateau between 0.7 and 0.8 μm, and then abruptly rise again to a value of 60 cm^{-1} at 0.66 μm.

This represents to our knowledge the first direct transmission measurement of the optical absorption coefficient of the deep bleachable absorbers in AlGaAs. Previously it has been primarily the cross section σ for optical ground- to metastable-state conversion that has been measured and assumed to be proportional to the absorption coefficient. We can test this, since

$$\sigma = (\tau\varphi)^{-1} \tag{5}$$

where the conversion rate, τ^{-1}, and a relative measure of the photon flux, φ, are also obtained in our experiment. Figure 6 presents σ (full triangles) versus λ. Clearly, σ and α_g indeed do have the same spectral dependence.

The conversion rate, τ^{-1}, can be estimated accurately from data such as that shown in figure 4 for values ranging from a few seconds to many minutes, giving accurate values of σ over many decades. The results, extending therefore over a much wider spectral range than available for the absorption coefficient, are plotted in figure 7. The full curve is the DX conversion cross section found in $Al_{0.37}Ga_{0.63}As$:Te from capacitance transients (from figure 4 of [19]). The points and curve agree well for $\lambda \geq 0.9$ μm, confirming that here our transients reflect the well established DX conversion only. For $\lambda \leq 0.8$ μm, however, the data and curve diverge significantly, revealing the onset of a second, more-rapidly bleaching absorber. The sudden increase in the bleachable absorption coefficient at 0.66 μm (figure 6) also supports this identification of a second bleaching process.

This unexpected and interesting result is currently under study. We have established, for example, that bleaching this shorter-wavelength band produces additional persistent photoconductivity and is the origin (figure 4) of the increased free-carrier absorption at 1.6 μm after white-light illumination. Preliminary experiments indicate also that recovery from this second bleaching process occurs at a somewhat lower temperature ($\sim$10 K lower) than does the DX bleaching process. We suspect that it may arise from an unrelated defect—metastable or simply compensating—in high concentration in our particular sample. We cannot rule out, however, that it is DX-related and simply missed by previous studies. We will defer further discussion concerning this source of additional persistent photoconductivity until our current studies are completed, and the results will be presented in a subsequent more detailed publication. For our purposes here, we can ignore this second bleachable stage and proceed with the results of MCD studies on the confirmed DX-related band at $\lambda >$ 0.9 μm.

Like the transmission, the MCD is also found to be time dependent after cooling the sample in darkness, but differs from the transmission in being magnetic field dependent. Figure 8 presents examples measured at 0.9 μm for fields of 0 and 1.9 T. At $B = 0$, the MCD is independent of time and serves to define the zero, as shown. At 1.9 T, MCD(t) increases from an initially finite, positive value to a steady-state value MCD(∞), identified as the free-carrier MCD.

Figure 9 presents the initial MCD versus B at 900, 1032 and 1250 nm. The circles (crosses) are 1.7 K (4.2 K) data. The long-dashed (short-dashed) lines are linear fits to the 1.7 (4.2 K) data. The slopes decrease rapidly with increasing wavelength, opposite to the free-carrier MCD spectral dependence, so any free-carrier contribution to the initial MCD is small. Hence, we identify the initial MCD with the DX ground state absorption.

The initial MCD shows no statistically significant temperature dependence. Taking the scatter as an upper limit for the possible paramagnetic contribution to the DX ground-state MCD, a value of $\leq$0.004% of the peak absorption coefficient (30 cm^{-1}) is found. Since fractional MCD (scaled to our temperature and field strength) of paramagnetic defects in semiconductors or insulators

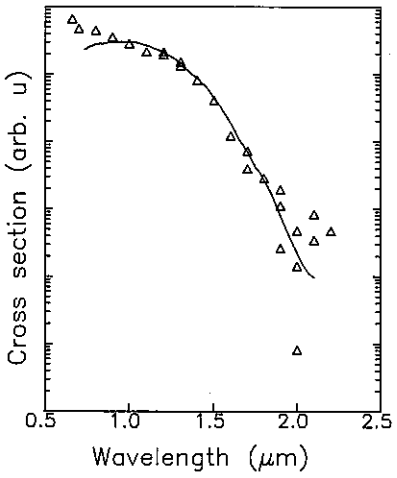

Figure 7. Spectral dependence of the conversion cross section for the bleachable absorbers. The smooth curve, from figure 4 of [19], is σ for DX centres in $Al_{0.37}Ga_{0.63}As$:Te.

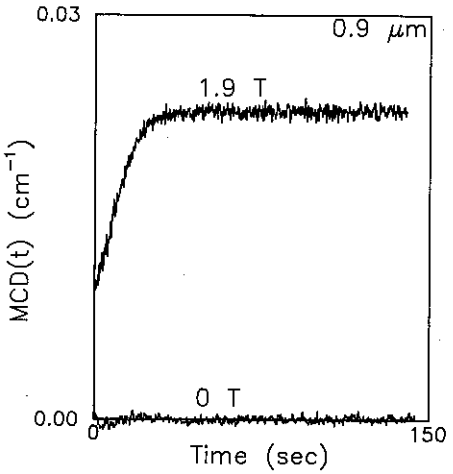

Figure 8. Transient MCD at 0.9 μm after cooling $Al_{0.35}Ga_{0.65}As$:Te to 1.7 K in the dark.

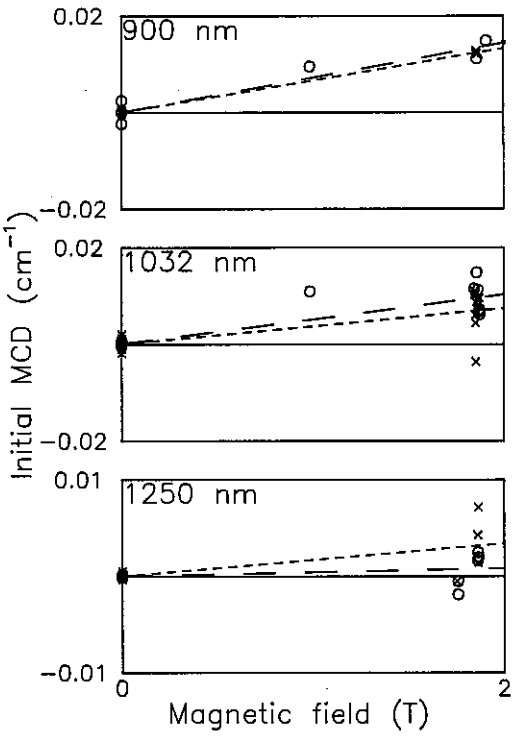

Figure 9. Initial MCD versus magnetic field at 900, 1032 and 1250 nm. Data measured at 1.7 K (4.2 K) are given by open circles (crosses) and fit by long-dashed (short-dashed) lines.

is often of the order of 0.1 to 10%, this result lends strong support to the diamagnetic ground state, negative-U model of Chadi and Chang.

It is important to point out, however, that it is not a *proof*. As pointed out in the introduction, the *detection* of a significant paramagnetic contribution would have served as a proof for a paramagnetic ground state. However, as in EPR, the *failure* to detect paramagnetism is not a proof of its absence. In the case of MCD, its strength is proportional to spin-orbit interaction in the final level of the optical absorption transition. We have no direct information of its magnitude and it could be small and strongly quenched by the low symmetry of the defect. Thus, the very low upper limit that we have established for the paramagnetic MCD component must be considered another strong 'nail in the coffin' for the neutral, paramagnetic, single-electron state model, but the 'coffin' is still not completely closed and should not yet be buried without a few more 'nails'.

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