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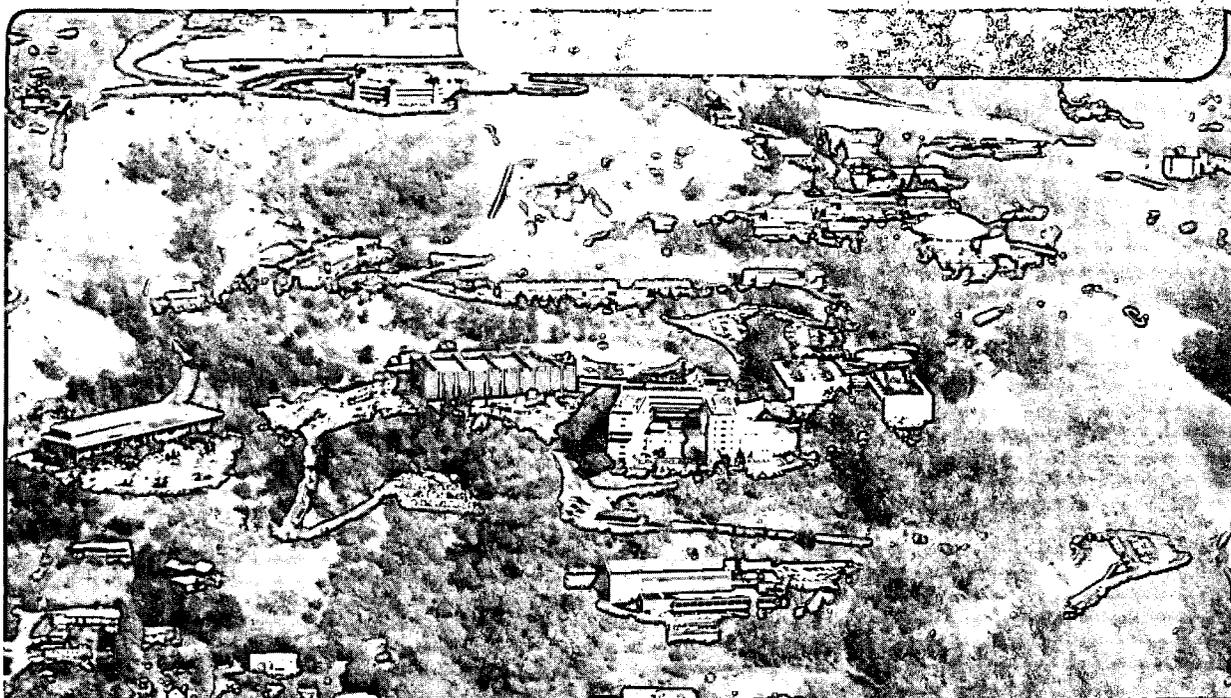
COPPER-DIHYDROGEN ACCEPTORS IN HIGH-PURITY GERMANIUM

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## COPPER-DIHYDROGEN ACCEPTORS IN HIGH-PURITY GERMANIUM\*

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We show that a coupled dynamic system of two hydrogen nuclei and a hole can bind to the trivalent acceptor copper in germanium. The result is a monovalent acceptor whose symmetry and electronic structure depend on hydrogen isotopic mass. The acceptor  $A(\text{CuH}_2)$  has tetrahedral symmetry and a complicated ground-state multiplet. All heavier isotope combinations exhibit only one ground-state level of reduced symmetry. These isotope-induced differences are interpreted in terms of the mass-induced rotation-libration transition of a hindered rotor.

In germanium, copper is a rapid interstitial diffuser as well as a substitutional triple acceptor. Copper forms several acceptor complexes with hydrogen and with lithium,<sup>1</sup> which have been observed using Hall effect, deep-level transient spectroscopy, and photothermal ionization spectroscopy (PTIS). A model was proposed in which each atom of hydrogen or lithium adds an electron to the copper's local bonding environment, reducing by one the acceptor's electrical valence. More recent measurements have shown that copper can be passivated by hydrogen,<sup>2</sup> and  $\text{CuH}_3$  was proposed as the resulting neutral species. We report here new PTIS measurements on acceptors near  $(E_V + 18 \text{ meV})$ , which we show to be copper-dihydrogen complexes. Using all three hydrogen isotopes (H, D, and T), we have investigated their electronic structure as a function of isotope content.

Complexes involving H and/or D were generated in samples from ultra-pure crystals grown in ambients of  $\text{H}_2$ ,  $\text{D}_2$  or 1:1  $\text{H}_2 - \text{D}_2$  mixtures; these crystals are known to contain  $\sim 10^{15} \text{ cm}^{-3}$  atoms of hydrogen isotopes. Copper plating was followed by annealing at  $400^\circ\text{C}$  for 24 h, sufficient to produce  $\sim 4 \times 10^{11} \text{ cm}^{-3}$  copper-dihydrogen acceptors. Centers involving T were generated in samples from crystals pulled in vacuum. After copper plating and annealing at  $500^\circ\text{C}$  for 24 h, they were exposed to 1 Torr plasmas of  $\text{T}_2$  or  $\text{H}_2 - \text{T}_2$  mixtures, at  $470^\circ\text{C}$  for 2 h.

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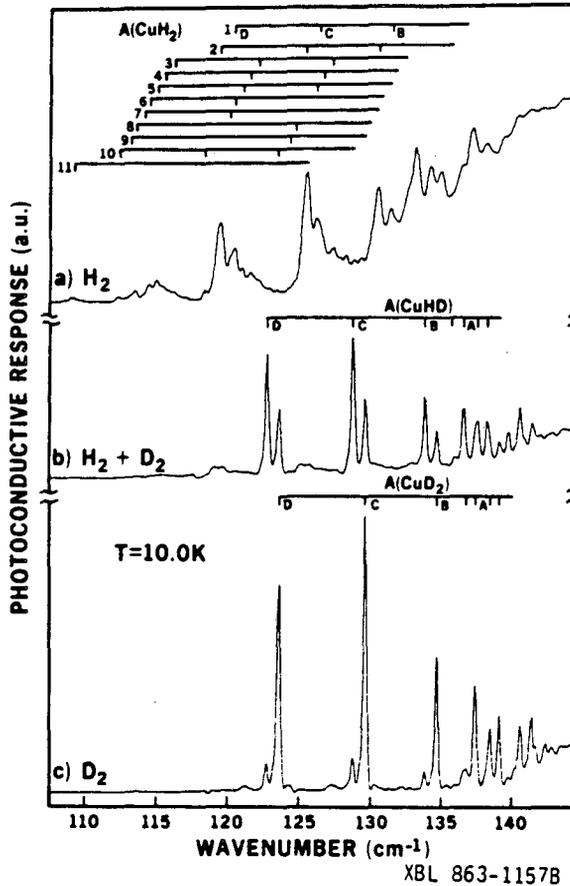


FIG. 1: Photothermal ionization spectra of copper-dihydrogen acceptors in samples grown in different ambients.

The PTI spectrum of a sample grown in a pure H<sub>2</sub> ambient is shown in Fig. 1(a). At least eleven overlapping hydrogenic line series are present. The study of their thermalization between 4.2 and 14 K shows that all series originate from the ground-state manifold of a single center. The sample of Fig. 1(c) was grown in a nearly pure D<sub>2</sub> atmosphere; its spectrum is dominated by one hydrogenic series at higher wavenumber than any seen in Fig. 1(a). The sample of Fig. 1(b) was grown in a 1:1 H<sub>2</sub> - D<sub>2</sub> mixture. Its spectrum includes the multiple line series of the center containing H, as well as the single series of the center containing D. But the spectrum is dominated by yet another hydrogenic line series, due to a center containing both H and D. Using the integrated peak areas of a given optical transition (where we include all the series from the center containing H), we find the following relative concentrations in the mixed-gas sample: [containing H]: [containing H,D]: [containing D] = 1:2:1. It immediately follows that the centers are A(CuH<sub>2</sub>),

A(CuHD) and A(CuD<sub>2</sub>) respectively. When vacuum-grown, copper-doped samples are exposed to plasmas of H<sub>2</sub> - T<sub>2</sub> mixtures, PTIS reveals yet another two line series. When we vary the relative amounts of H and T in the samples, the relative amplitudes of the two new series indicate that they arise from A(CuHT) and A(CuT<sub>2</sub>).

For the five copper-dihydrogen acceptors which have been identified, Fig. 2 shows a plot of the binding energies versus the reciprocal reduced mass of the two hydrogen nuclei. The acceptors A(CuHD), A(CuHT), A(CuD<sub>2</sub>) and A(CuT<sub>2</sub>) display a remarkably monotonic dependence of binding energy on this quantity. This is strong evidence that the isotope shifts relate to motion of the nuclei.

We studied the acceptor A(CuD<sub>2</sub>) under uniaxial stresses applied parallel to [111], [100] and [110]; the stress-dependent energy shifts of the D-lines are shown in Fig. 3. The behavior of the final-state level is identical to that of a Group III acceptor.<sup>3</sup> For each stress direction, the ground-state level evolves into two levels. The ratios of the shifts experienced by the higher-energy level, to those of the lower-energy level, are  $1.07 \pm 0.07$ ,  $1.82 \pm 0.09$ , and  $4.94 \pm 0.21$  for the respective directions. These shifts do not arise solely from lifting of

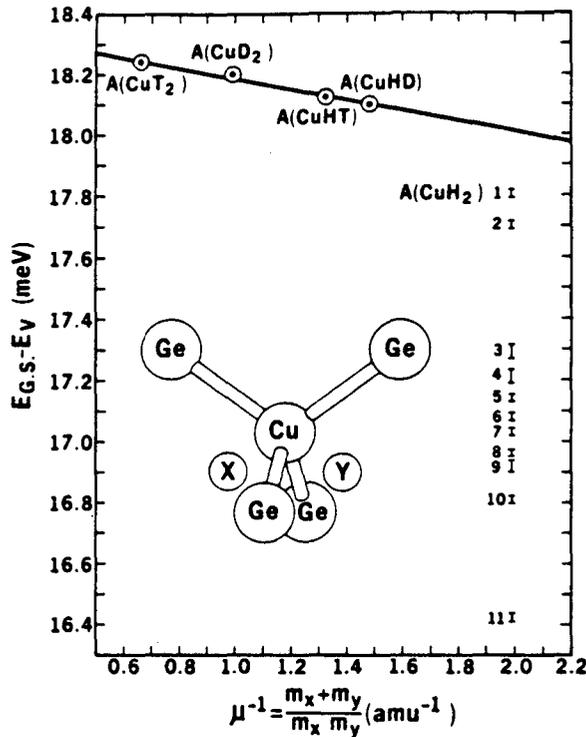


FIG. 2: Binding energies of copper-dihydrogen acceptors versus reciprocal reduced mass of the two hydrogen nuclei x and y. Inset: schematic structure of the copper-dihydrogen centers.

Despite its asymmetric internal structure. Under stress along [111], the level  $A(CuH_2)_1$  splits into two levels whereas  $A(CuH_2)_2$  does not split. Because  $T_d$  contains both orbitally degenerate and orbitally nondegenerate double-valued representations, this behavior is consistent with tetrahedral symmetry.

We can qualitatively explain the isotope-induced differences among the various copper-dihydrogen acceptors in terms of the Devonshire model.<sup>7</sup> That model treats the energy levels of a rigid rotor hindered by a potential of octahedral symmetry, which may have either trigonal or tetragonal minima. A copper-dihydrogen complex constitutes a rotor moving in a tetrahedral potential; the direction of potential minima are not known. We observe the nuclear motion indirectly, via its effect on the acceptor electronic states. Despite these differences, the Devonshire model provides useful insight into the acceptors we study here.

The  $A(CuH_2)$  complex corresponds to a hindered rotor of low moment of inertia, whose energy levels resemble those of a free rotor. The protons move so rapidly that optical transitions are unable to measure them as localized in any of the potential minima. What results is an acceptor of tetrahedral symmetry, with a ground state split into a complicated multiplet. The copper-dihydrogen complexes which include

electronic degeneracy, since they are inconsistent<sup>3</sup> with the behavior of a  $T_g$  level in the group  $T_d$ . The shifts cannot be fitted to the piezospectroscopic constants for any known class of reduced symmetry.<sup>4</sup> Nonetheless, the observed shifts must derive, at least in part, from the lifting of orientational degeneracy.

In contrast to the other copper-dihydrogen acceptors,  $A(CuH_2)$  has a complicated manifold of 1s-like states, none of which fits the mass-dependent systematics exhibited by the others (see Fig. 2). The two protons in  $A(CuH_2)$  possess a dynamic degree of freedom unavailable to the other isotope combinations: the H-Cu-H system is light enough to rapidly tunnel among several equivalent potential energy minima.<sup>5</sup> This motion splits the ground state into a complicated multiplet structure, much like that observed for the dynamic  $D(LiO)$  donor complex.<sup>6</sup> Another effect of this rapid tunneling is to give  $A(CuH_2)$  tetrahedral symmetry des-

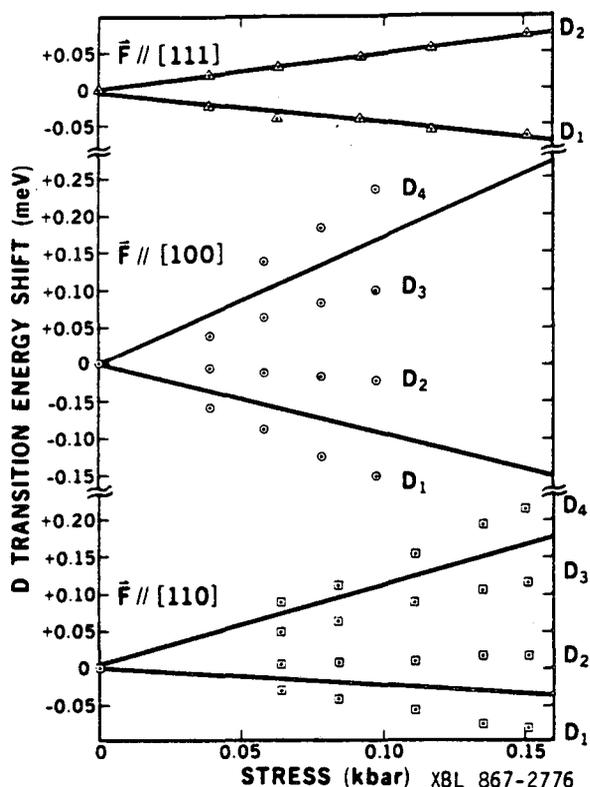


FIG. 3: Energy shifts of the  $A(\text{CuD}_2)$  D-line under uniaxial stress. Points  $D_1, \dots, D_4$  are observed peak positions. Heavy lines indicate shifts of the ground-state levels; the final-state splittings  $D_4 - D_3 = D_2 - D_1$  are observed for  $[100]$  and  $[110]$ .

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heavier nuclei can be understood as hindered rotors of higher moments of inertia, for which the lowest states form closely-spaced librational levels. The near-degeneracy of librational levels means that motion of the nuclei between potential minima is slow, and the nuclei appear localized by the process of an optical transition. These acceptors therefore display symmetry lower than tetrahedral: Their binding energies exhibit monotonic isotope shifts, caused by mass-induced changes in the frequency of zero-point libration, coupled coulombically to the bound hole.<sup>8</sup> The residual effects of tunneling may be responsible for the failure of  $A(\text{CuD}_2)$  to fit any known symmetry class.

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