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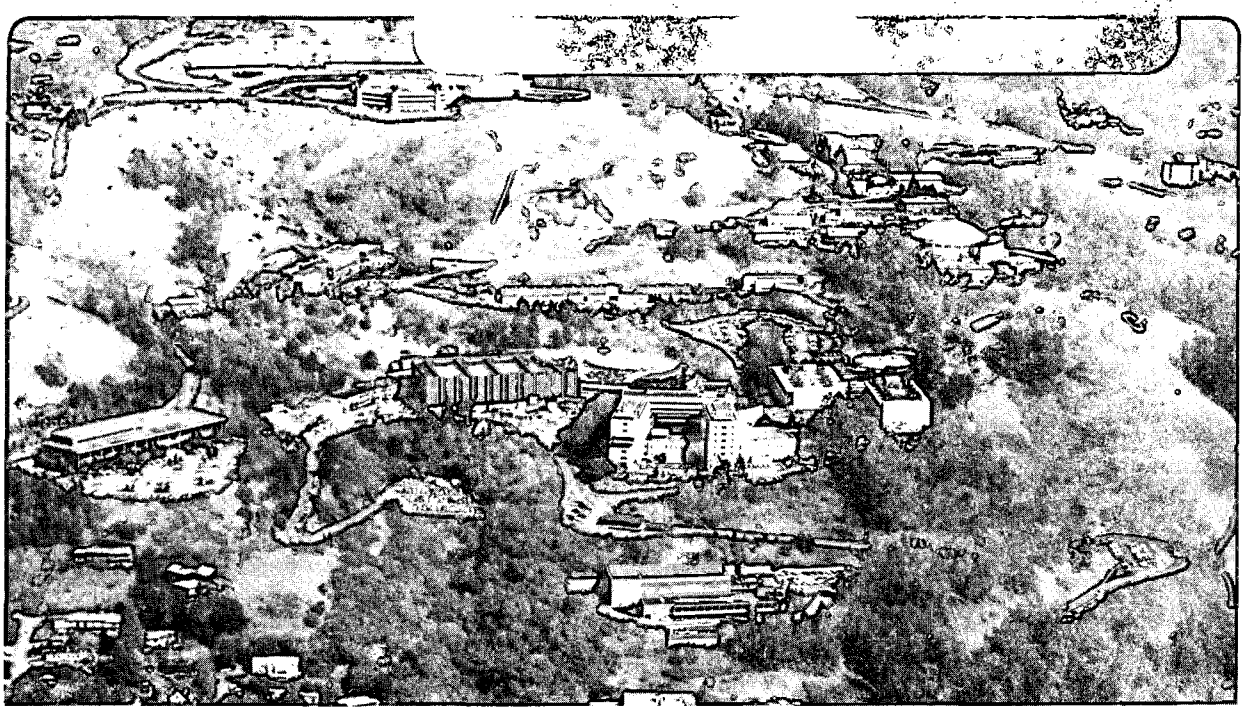

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Isotope-Induced Symmetry Change in Dynamic Semiconductor Defects

J. M. Kahn[a], L. M. Falicov[a], and E. E. Haller[b]

University of California and Lawrence Berkeley Laboratory, Berkeley, CA 94720

Two hydrogen nuclei and a hole bind to the triple-acceptor copper in germanium. The result is a single acceptor whose electronic states are modified by coupling to the zero-point motion of the nuclei. That motion displays a qualitative change from rotation to libration induced by an increase in hydrogen isotopic mass. The acceptor $A(CuH_2)$ has full tetrahedral symmetry and a complex ground-state manifold. All heavier isotope combinations display only a single ground-state component of symmetry lower than tetrahedral.

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Donor or acceptor complexes which include light nuclei, such as hydrogen or lithium, can possess electronic properties which are modified by coupling to the zero-point motion of the nuclei.[1] In ultrapure germanium, the donor D(H,O) and the acceptor A(H,Si) exhibit small shifts in their zero-phonon spectrum upon deuteration,[2,3] caused by a reduction in the frequency of nuclear motion. The donors D(H,O) and D(Li,O) appear in optical experiments[3,4] to possess tetrahedral symmetry despite their asymmetric internal structure. The rapid tunneling of light nuclei among several equivalent orientations effects this recovery of high symmetry and modifies the donor electronic ground state; the result is a manifold of states with unusual behavior under uniaxial stress.

In germanium, copper is a rapid interstitial diffuser[5] as well as a substitutional triple acceptor.[6] Copper forms several acceptor complexes with hydrogen and with lithium,[7,8] which have been observed using Hall effect, deep-level transient spectroscopy, and photothermal ionization spectroscopy[9] (PTIS). A model was proposed[7] in which each atom of hydrogen or lithium adds an electron to the copper atom's local bonding environment, reducing by one the acceptor's electrical valence.[10] Copper can be completely passivated by hydrogen,[11,12] and CuH_3 has been proposed as the resulting neutral species. In this letter, we report new PTIS measurements on acceptors near (E_v + 18 meV), which we show to be copper-dihydrogen complexes.

To investigate centers involving H and/or D, we took samples from ultrapure crystals grown in ambients of H_2, D_2 or 1:1 H_2 - D_2 mixtures; these crystals are known to contain 0.5 to 2.0 x 10^{15} cm^{-3} atoms of hydrogen isotopes.[13] Copper plating was followed by annealing at 400°C for 24 h, sufficient to produce about 4 x 10^{11} cm^{-3} copper-dihydrogen acceptors.[7] For studies of centers involving tritium (T), we began with samples from crystals pulled in vacuum. After copper plating and annealing at 500°C for 24 h, these samples were treated in 1 Torr plasmas of T_2 or H_2 - T_2 mixtures, at 470°C for 2 h.

The PTI spectrum of a sample grown in a pure H_2 ambient is shown in Fig. 1(a). At least eleven overlapping hydrogenic line series are present. Comparison of spectra taken between 4.2 and 14 K shows that at higher temperatures, series at a lower wavenumber become relatively stronger, consistent with a single center which has a manifold of 1s-like states. The sample of Fig. 1(c) was grown in a nearly pure D_2 atmosphere. Its spectrum is dominated by one hydrogenic series of lines which does not match any series observed in samples grown in H_2. The sample of Fig. 1(b) was grown in a 1:1 mixture of H_2 and D_2. Its spectrum contains the multiple line series of the center containing H, as well as the single line 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. We estimate the relative concentrations of the three centers by comparing integrated peak areas of the D or C transition, where we include all the series of the center containing H. We find the following relative concentrations: [containing H]:[containing H,D]:[containing D] = 1:2:1. It immediately follows that the centers are $A(CuH_2)$, A(CuHD), and $A(CuD_2)$ respectively. Given an equal number of H and D atoms, there are twice as many ways to make HD as either H_2 or D_2. Reexamination of Fig. 1(c) shows that the sample contains a small amount of A(CuHD), caused by traces of H in the D_2 gas used during crystal growth.

When hydrogen-free, copper-doped samples are exposed to plasmas of H_2 - T_2 mixtures, yet another two line series are observed, with energies slightly higher than A(CuHD) and $A(CuD_2)$ respectively. When we vary the relative amounts of H and T in the samples, the relative amplitudes of the two new series indicate that they are due to A(CuHT) and $A(CuT_2)$.

In Table I, we summarize the binding energies of the five copper-dihydrogen acceptors which have been unambiguously identified. Figure 2 shows a plot of

the binding energies versus the reciprocal reduced mass of the two hydrogen nuclei:

$$\mu^{-1} = \frac{m_x + m_y}{m_x m_y}$$

with x, y = H, D, T. The acceptors A(CuHD), A(CuHT), A(CuD_2) and A(CuT_2) display a remarkably monotonic dependence of binding energy on this quantity. This is strong evidence for a relationship between isotope shift and motion of the nuclei.

The acceptor A(CuD_2) was investigated under uniaxial compressional stresses of up to 0.15 kbar, applied parallel to [111], [100], and [110]. We analyzed in detail the D line, and found that the final-state level evolves into 1, 2, and 2 levels for the respective stress directions. This behavior is indistinguishable from that of a normal elemental acceptor.[15] For each stress direction the ground-state level of A(CuD_2) evolves linearly with stress into two levels, resulting in the observation of 2, 4, and 4 D-lines for the respective stress axes.[16] The ground-state shifts are given in Table II. These shifts do not arise solely from the lifting of electronic degeneracy, since they are inconsistent[17] with the behavior of a Γ_8 state in the group $\overline{T}_d$. They cannot be fitted to the piezospectroscopic constants for any known class of lowered symmetry.[18] The best fit is to Rhombic I symmetry, but even in that case, the sign of the shifts for [100] and [110] are inconsistent with each other. Nonetheless, the observed shifts must derive, at least in part, from a set of differently oriented centers whose energies shift differently under stress.

Unlike the other copper-dihydrogen acceptors, A(CuH_2) has a complicated manifold of 1s-like states, none of which fits the systematic dependence on mass exhibited by the others (see Fig. 2). It is unlikely that the extra states originate from a bonding structure that is very different from the

other acceptors. It is also not likely that the various states are caused by the existence of several different static configurations of the two protons, each resulting in different electronic energy for the bound hole, since it is difficult to imagine so many equilibrium configurations which are not equivalent under operations of the tetrahedral group. The splittings are far too large to originate from hyperfine effects of the protons, and cannot be explained solely on the basis of any mechanism involving nuclear spin, since $A(CuT_2)$ also includes two identical spin 1/2 hydrogen nuclei. We conclude that in $A(CuH_2)$, the protons possess some dynamic degree of freedom qualitatively different from those available to other isotope combinations. We believe that the light reduced mass of the H-Cu-H system allows it to tunnel rapidly among several equivalent potential energy minima.[3] This tunneling splits the ground state into a complex manifold, much like the many levels observed for the dynamic D(Li,O) donor complex.[4]

A consequence of such rapid tunneling would be the recovery of tetrahedral symmetry. Given the complex overlapping structure of its spectrum, piezospectroscopy of $A(CuH_2)$ has been possible only for stress along [111], where splitting of bound excited states is negligible. Figure 3 shows the behavior of the D lines of the two lowest states $A(CuH_2)_1$ and $A(CuH_2)_2$, at stresses up to 0.30 kbar. The acceptor level $A(CuH_2)_1$ splits into two components of equal intensity, and beyond ~ 0.10 kbar, each component moves with a slope of about ± 0.35 meV/kbar. In contrast, $A(CuH_2)_2$ does not split. Observing that the group $\overline{T}_d$ contains both orbitally degenerate (Γ_8) and orbitally nondegenerate (Γ_6 and Γ_7) double-valued representations, we conclude that $A(CuH_2)$ possesses tetrahedral symmetry.[19] The somewhat nonlinear behavior of $A(CuH_2)_1$ and $A(CuH_2)_2$ may arise from interaction with other states in the manifold (whose overlapping peaks were not resolved), or from the effect of stress on the motion of the protons.

The isotope-induced differences among the various copper-dihydrogen acceptors can qualitatively be understood in terms of the Devonshire model.[20,21] That model treats the energy levels of a hindered rigid rotor moving in a potential of octahedral symmetry, having either trigonal or tetragonal minima. As the rotor's moment of inertia is increased, its motion exhibits a qualitative change from rotational to librational character. In the acceptors we study here, the copper dihydrogen complex constitutes a rotor moving in a tetrahedral potential; the directions of potential minima are not known, since we have been unable to determine the symmetry of $A(CuD_2)$. Our experiments observe the motion of the nuclei indirectly, through its effect on the spectrum of electronic acceptor states. The Devonshire model provides a useful insight into this somewhat different problem.

The $A(CuH_2)$ complex, with two protons, can be understood as a hindered rotor of low moment of inertia, whose energy levels resemble those of a free rotor. The zero-point motion of the two protons is so rapid on the time scale of optical transitions that those transitions are unable to measure the protons as localized in any of the potential minima. The result is an acceptor of tetrahedral symmetry, with an electronic ground state split into a complex manifold.[3,4] The copper-dihydrogen acceptors which include heavier nuclei correspond to rotors of greater moment of inertia, for which the lowest few states form closely-spaced librational levels, separated by the so-called tunnel splitting. Under certain circumstances (e.g., tetragonal minima in the Devonshire model), the tunnel splitting becomes very small, approaching zero exponentially in the limit of high moment of inertia. The near-degeneracy of librational levels means that tunneling of the nuclei between their potential minima is slow; the nuclei are localized by the measurement process of an optical transition. The result is that each one of these acceptors displays symmetry lower than tetrahedral. Their ground-state energies exhibit monotonic

isotope shifts, caused by mass-induced changes in the frequency of zero-point libration, electrostatically coupled to the bound hole.[22] It is possible that the residual effects of tunneling are responsible for the failure of the piezospectroscopic constants of $A(CuD_2)$ to fit any known symmetry class.

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(a) Department of Physics.

(b) Department of Materials Science and Mineral Engineering.

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[19]The splittings cannot be explained in terms of purely orientational degeneracy. One might assume that (a) $A(CuH_2)$ had $\overline{D_{2d}}$ symmetry, which exhibits no orientational splitting for [111] stress; (b) $A(CuH_2)_1$ was two degenerate Kramers doublets (X_6 and/or X_7); and (c) $A(CuH_2)_2$ was one such doublet. Those assumptions would, however, provide no explanation for the origin and multiplicity of the ground-state manifold.

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TABLE I. Binding Energies[c] of Copper-Dihydrogen Acceptors

Acceptor Level	$E - E_V$ (meV)	Uncertainty (meV)
$A(CuH_2)_1$	17.81	0.01
$A(CuH_2)_2$	17.70	0.01
$A(CuH_2)_3$	17.29	0.02
$A(CuH_2)_4$	17.21	0.02
$A(CuH_2)_5$	17.14	0.01
$A(CuH_2)_6$	17.08	0.01
$A(CuH_2)_7$	17.03	0.01
$A(CuH_2)_8$	16.96	0.01
$A(CuH_2)_9$	16.92	0.02
$A(CuH_2)_{10}$	16.81	0.01
$A(CuH_2)_{11}$	16.42	0.01
A(CuHD)	18.098	0.002
A(CuHT)	18.123	0.002
$A(CuD_2)$	18.201	0.002
$A(CuT_2)$	18.239	0.002

[c]Taken as energy of the D transition plus 2.880 meV. [See Ref. 14.]

Table II. Stress-Induced Shifts[d] of the $A(CuD_2)$ Ground-State Level

Stress Direction	Shifts (meV/kbar)		Shift Ratios
[111]	+ 0.46 ± 0.02	- 0.43 ± 0.02	1.07 ± 0.07
[100]	+ 1.697 ± 0.009	- 0.93 ± 0.05	1.82 ± 0.09
[110]	+ 1.07 ± 0.04	- 0.217 ± 0.004	4.94 ± 0.21

[d]Variously oriented defects shift in different directions. The numbers given are the shifts of hole binding energies. The errors given reflect scatter of the data points. Because of the stress calibration used, the shift magnitudes for the various stress directions are subject to uncertainties of 2, 4, and 7% respectively. Those errors do not affect the accuracy of the shift ratios.

FIGURE CAPTIONS

FIG. 1: Photothermal ionization spectra of copper-dihydrogen acceptors in samples grown in different ambients. (a) Pure H_2, containing $A(CuH_2)$; (b) 1:1 mixture of H_2 and D_2, containing $A(CuH_2)$, A(CuHD), and $A(CuD_2)$ in a 1:2:1 ratio; (c) nearly pure D_2, containing $A(CuD_2)$ and a trace of A(CuHD).

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, viewed slightly off a <110> direction.

FIG. 3: Energy of the D transitions of $A(CuH_2)_1$ and $A(CuH_2)_2$, under [111] uniaxial stress. Dashed lines are provided only to guide the eye.

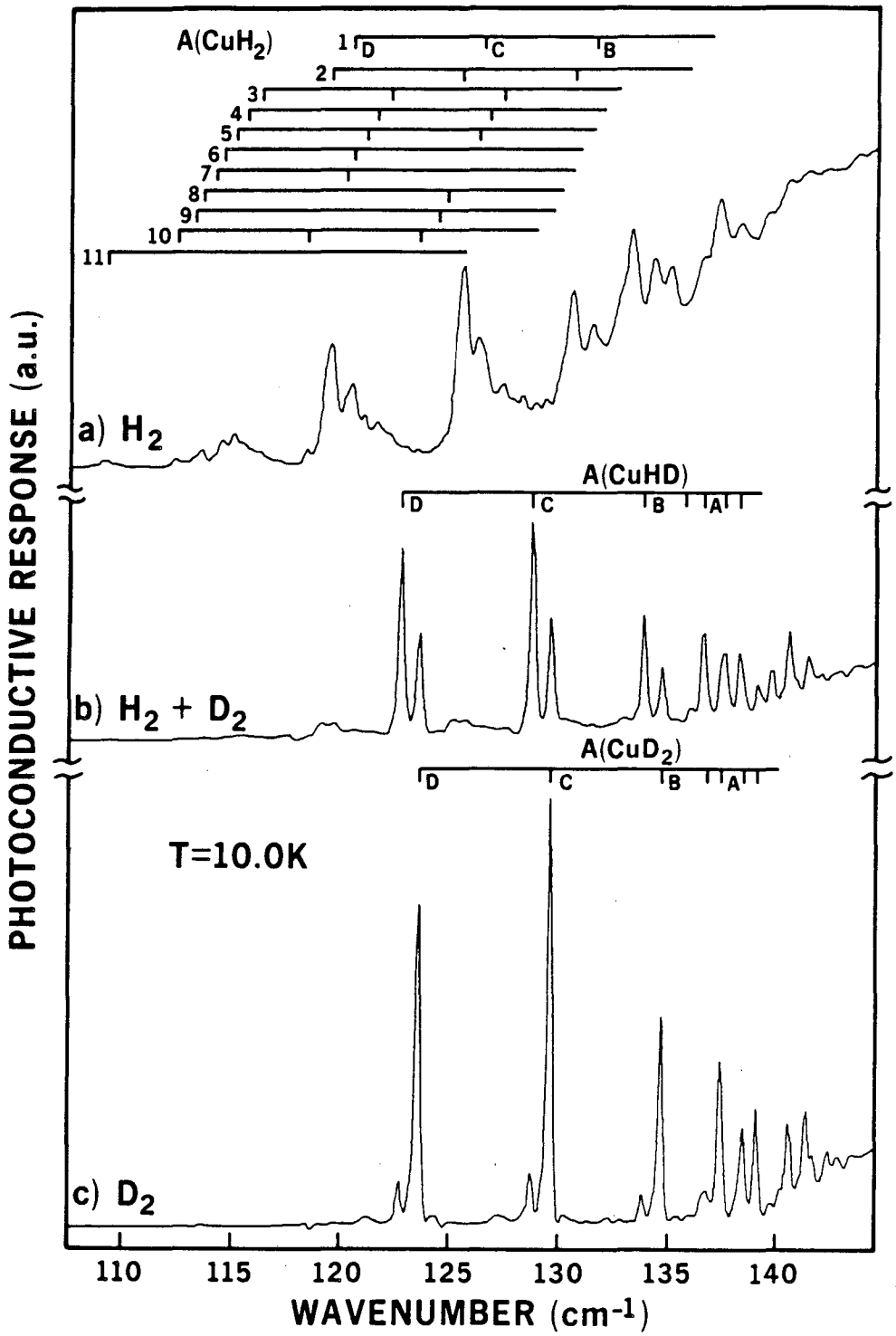

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Fig. 1.

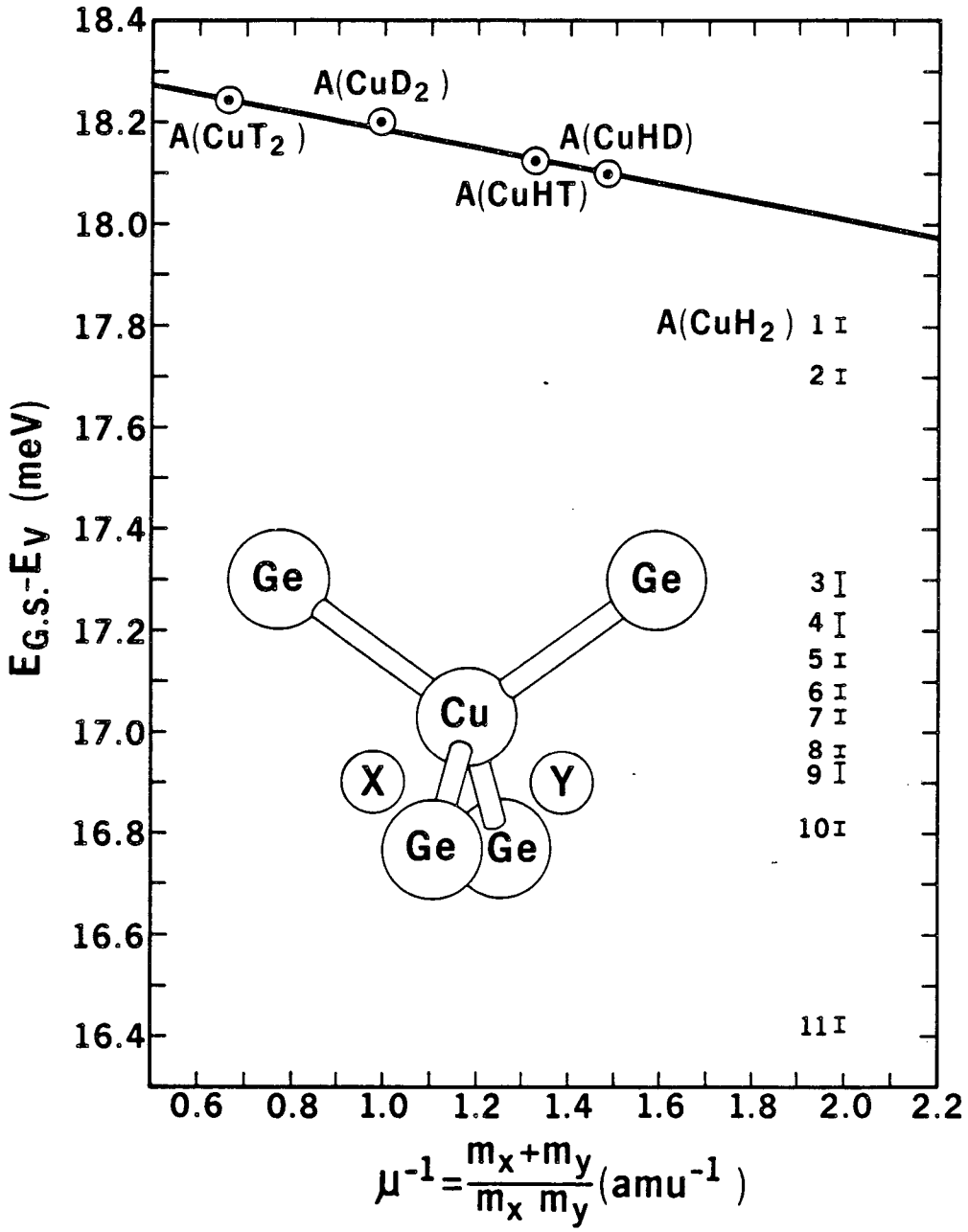

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Fig. 2.

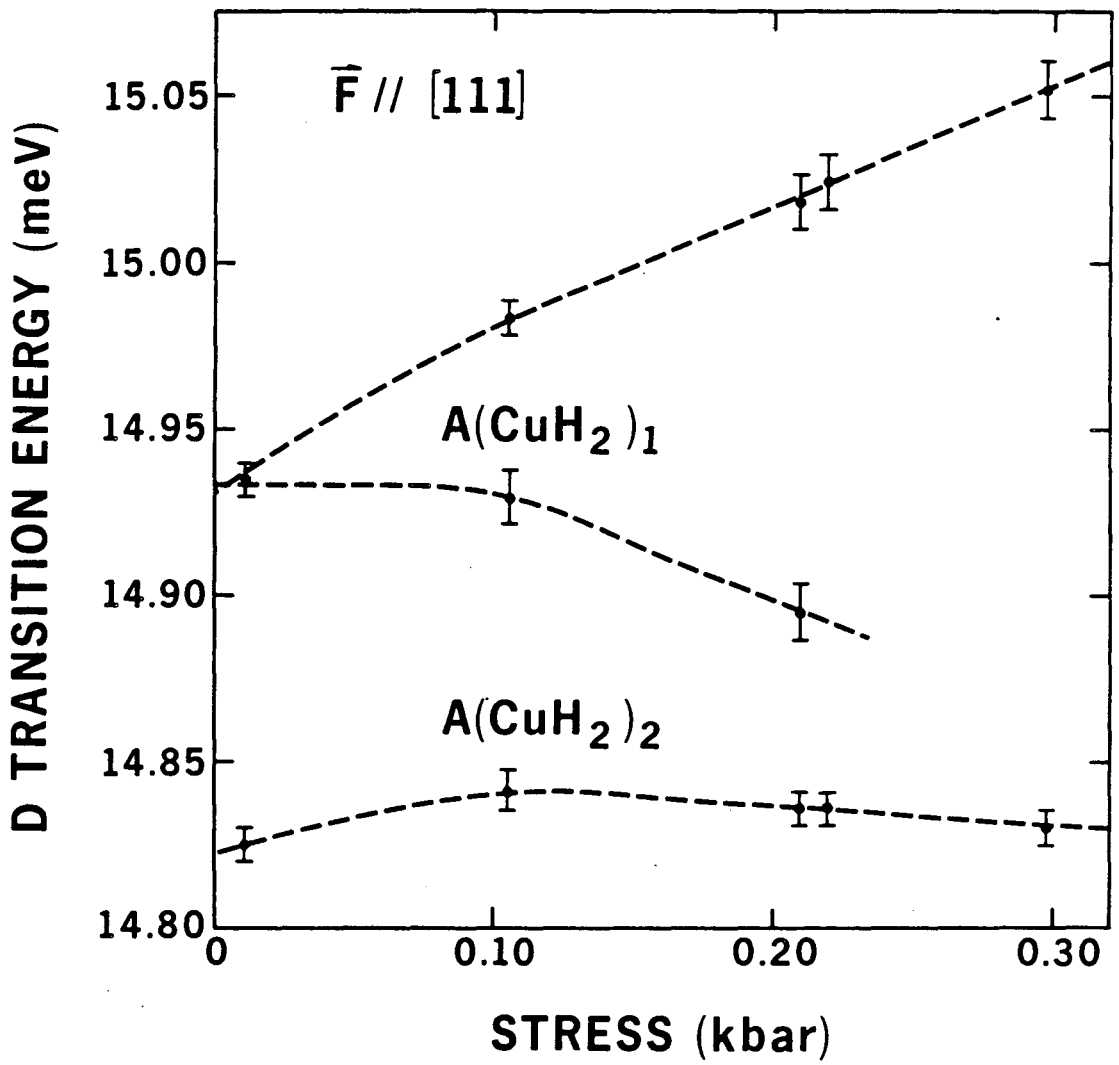

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Fig. 3.

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