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HIGH-PURITY GERMANIUM

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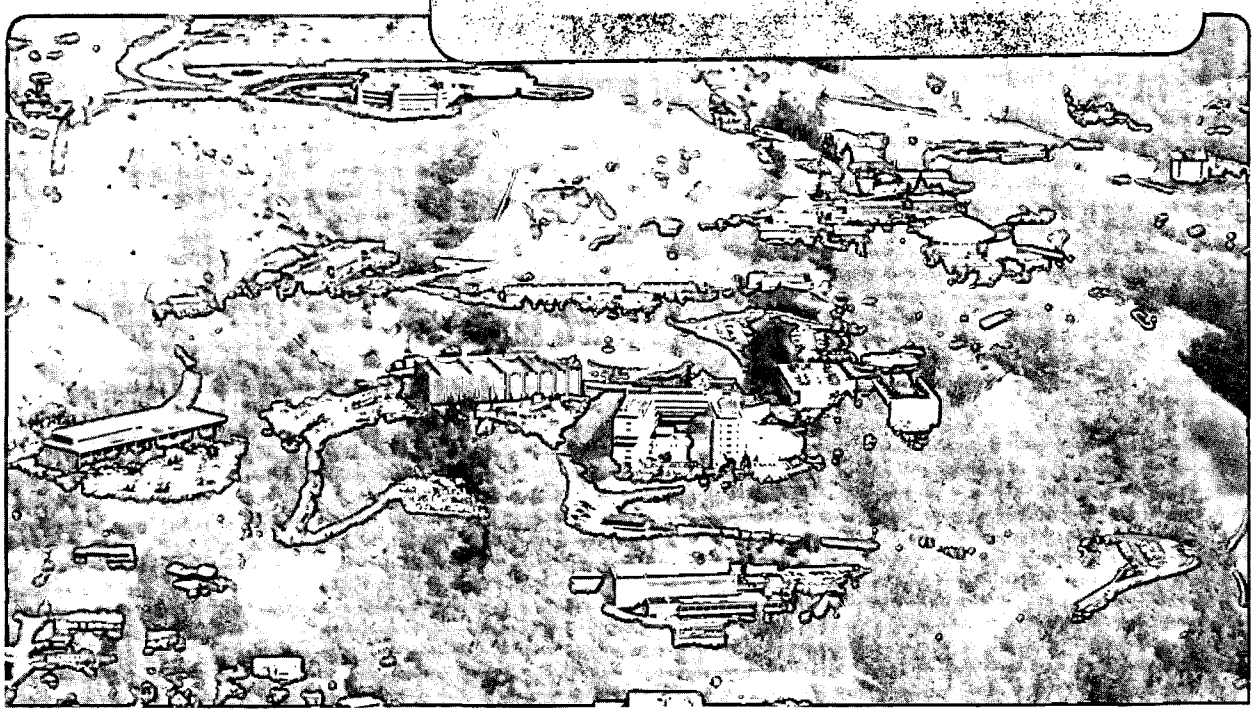

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Copper-Dihydrogen Acceptors in High-Purity Germanium

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Copper-dihydrogen complexes have been found to form shallow acceptors in germanium. These acceptors are strongly coupled dynamic systems of two nuclei and a hole, bound at a tetrahedral Cu^{3-} site. As a result, the electronic structure depends on the hydrogen isotopic mass. The acceptor $A(CuH_2)$ has a complicated ground-state manifold of at least eleven states. In sharp contrast, A(CuHD), A(CuHT), $A(CuD_2)$ and $A(CuT_2)$ each exhibit only a single ground-state component.

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The interaction of hydrogen with acceptors in crystalline semiconductors has received considerable recent attention. Detailed bonding arrangements, and the electronic structure of acceptor-hydrogen complexes, vary from case to case. An emerging common feature is that the hydrogen atom adds its electron to the acceptor's local bonding environment, reducing by one the acceptor's electronic valence.

Group III acceptors in silicon are neutralized by the addition of a hydrogen atom.[1-3] For boron, the proposed neutral complex involves a threefold-coordinated boron atom adjacent to a broken Si-B bond that has been capped by the hydrogen atom.[4,5] A similar bonding mechanism has been proposed to explain the observed neutralization of zinc acceptors in GaAs.[6] The Group II elements zinc and beryllium form double acceptors in germanium, and the addition of hydrogen converts these to the single acceptors A(Zn,H) and A(Be,H).[7] It was proposed that an atom of hydrogen donates its electron to the doubly-deficient bonds of the fourfold-coordinated Group II atom. The zero-point motion of the resulting proton involves a sampling of several equivalent nearby interstitial positions. Coupling of that motion to the bound hole radically alters the acceptor's electronic ground state.[8]

In germanium, the Group I element copper is a rapid interstitial diffuser[9] as well as a substitutional triple acceptor.[10] This acceptor can be passivated by hydrogen,[11,12] and CuH_3 has been proposed as the resulting neutral species. Copper also forms several electrically active acceptor complexes with hydrogen and with lithium,[13,14] which have been observed using Hall effect, deep-level transient spectroscopy, and photothermal ionization spectroscopy (PTIS).[15] In this letter, we report new PTIS measurements[16] on the acceptors near (E_v + 18 meV), which we show to be copper-dihydrogen complexes. These are the first shallow acceptors

involving two dynamic hydrogen nuclei which interact with the bound hole. The electronic ground state is altered in a way which exhibits a remarkable dependence on the specific hydrogen isotopes contained in the complex.

In this study, all samples initially had a net excess of shallow donors ($N_D - N_A = 0.5$ to 2.0×10^{11} cm^{-3}). To investigate centers involving H and/or D, samples were taken from 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 2.0×10^{15} cm^{-3} atoms of hydrogen isotopes.[17] Samples were copper plated and heated to 400°C for 24 h, sufficient to produce about 4×10^{11} cm^{-3} copper-dihydrogen acceptors.[13] For studies of centers involving T, we began with samples from crystals pulled in vacuum, which are free of hydrogen. Samples were copper plated and heated to 500°C for 24 h. They were then treated in plasmas of pure T_2 or T_2-H_2 mixtures, at a pressure of 1 Torr. Typical treatments of 470°C for 2 h were sufficient for T to diffuse about 0.5 mm into the samples.[18] Some samples received additional exposures to plasmas of H or D under similar conditions. All spectra were taken using a Fourier spectrometer, with an instrumental linewidth about three times narrower than any observed peaks of copper-dihydrogen centers.

The PTI spectra from a sample grown in a pure H_2 ambient are shown in Figure 1. At least eleven overlapping line series are present; there is no evidence for non-hydrogenic spacing within any series. Comparison of spectra at 6, 10 and 14 K shows that at higher temperatures, line series at lower energies become relatively stronger. This is consistent with a single center which has a manifold of states associated with its 1s-like envelope function.[8] We call this center $A(CuH_2)$ and justify that compositional assignment below. Only the lowest state $A(CuH_2)_1$ is occupied at zero temperature, but at finite temperature other states are occupied according to Boltzmann statistics. Analysis

of the more prominent D and C transitions shows consistent qualitative agreement with those statistics, but the overlapping structure of the spectra makes difficult a quantitative analysis. Additional evidence that all line series originate from one center is the fact that separately prepared samples from different crystals give spectra virtually identical to those in Fig. 1, provided the samples are sufficiently free of strain. Even in the absence of appreciable strain, the peaks of several line series show a symmetrical, temperature-independent broadening to widths of ~ 0.7 cm^{-1}, compared with the ~ 0.3 cm^{-1} widths characteristic of the other $A(CuH_2)$ series, and of the other copper-dihydrogen centers. This broadening may result from the presence of two or more closely spaced states.

Figure 2 shows that for different isotopes of hydrogen, strikingly different spectra of copper-dihydrogen acceptors are observed. The sample of Fig. 2(c) was grown in a nearly pure D_2 atmosphere. Its spectrum is dominated by a single hydrogenic line series which does not match any of the series observed in samples grown in H_2 [see Fig. 2(a)]. The sample of Fig. 2(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 single hydrogenic line series, presumably due to a center containing both H and D. The relative concentrations of the three centers can be estimated by comparing the integrated peak areas of a given transition (e.g., D or C), where we include all the series originating from the center containing H. We find the following relative concentrations: [containing H]:[containing H, D]:[containing D] ≈ 1:2:1. Immediate identification follows: 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. Examination of Fig. 2(c) shows that that 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 roughly 1:1 mixtures of H_2 and T_2, yet another two line series are observed, as shown in Fig. 3(b). These two series appear at slightly higher energy than A(CuHD) and A(CuD_2), which are shown for comparison in Fig. 3(a). 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) respectively. Both spectra in Fig. 3 also contain the multiple series due to A(CuH_2). When samples which contained both D and T were prepared, the PTI spectra exhibited a single broad series of peaks which straddled the positions of A(CuD_2) and A(CuT_2). Though the center A(CuDT) was almost certainly present, no new peaks could be resolved, indicating that A(CuDT) probably lies in energy between A(CuD_2) and A(CuT_2).

In Table I, we summarize the binding energies of the five copper-dihydrogen acceptors which have been unambiguously identified. For the four acceptors with single ground-state components, no associated states have ever been observed. Assuming any such states to have degeneracies and transition probabilities equal to those of the observed ground states, they must lie at least 5 meV shallower to escape detection.

Preliminary experiments involving uniaxial stress indicate that the centers A(CuHD) and A(CuD_2) have tetrahedral symmetry; their ground states exhibit the electronic splitting[20] characteristic of the Γ_8 representation of the group $\overline{T}_d$. We have insufficient data to determine the symmetries of the various states of A(CuH_2). As mentioned above, its spectrum is very sensitive to stress unintentionally applied to the sample.

Figure 4 shows a plot of the binding energy of the various copper-dihydrogen acceptors 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 systematic dependence of binding energy on this quantity. Their ground state energies are fitted with 0.001 to 0.014 meV by the expression:

$$E - E_v \text{ (meV)} = 18.3641 - 0.17796\ \mu^{-1}$$

for μ in amu. This is strong evidence for a relationship between the isotope shift and motion of the nuclei.

We model the acceptors as shown in the inset of Fig. 4. The copper atom is fourfold coordinated, and two atoms of hydrogen add their electrons to the triply-deficient bonds. The result is a monovalent acceptor, consistent with our observation of hydrogenic spacing in all line series. The two hydrogen nuclei are bound near the Cu^{3-} site, but their zero-point motion involves the sampling by each of at least four equivalent interstitial positions. The nuclear motion is coupled electrostatically to the bound hole, so that mass-induced changes in that motion are reflected as shifts in the acceptor binding energy. Heavier isotope combinations are less mobile, and perhaps less able to screen dynamically the Cu^{3-} potential seen by the bound hole; this might explain the sign of the mass-induced shifts. It is interesting to note that for a free-space diatomic molecule, the rotational energy quantum is proportional to the reciprocal reduced mass. The details of the actual nuclear motion are not yet known, but it must involve the sampling by each nucleus of at least four equivalent positions, rather than the vibration of each nucleus

about a single point of equilibrium. The latter type of motion was successfully invoked to explain the mass-dependent isotope shifts of zero-phonon optical transitions of nitrogen-pair electron traps in GaP.[21] However, in the present case, at least four vibrating hydrogen atoms would be required to produce a center with tetrahedral symmetry.

Reference to Fig. 4 shows that $A(CuH_2)$ represents a puzzling anomaly. Its ground state energy does not at all fit the systematics demonstrated by the other four acceptors. And unlike the others, $A(CuH_2)$ has a manifold of associated 1s-like states, widely dispersed in energy. An explanation of these anomalies--and of the systematic behavior exhibited by the other four acceptors--must await a detailed theory.

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

Acceptor Level	$E - E_V$ (meV)	Uncertainty (meV)
$A(CuH_2)_1$	17.80	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. 19.]

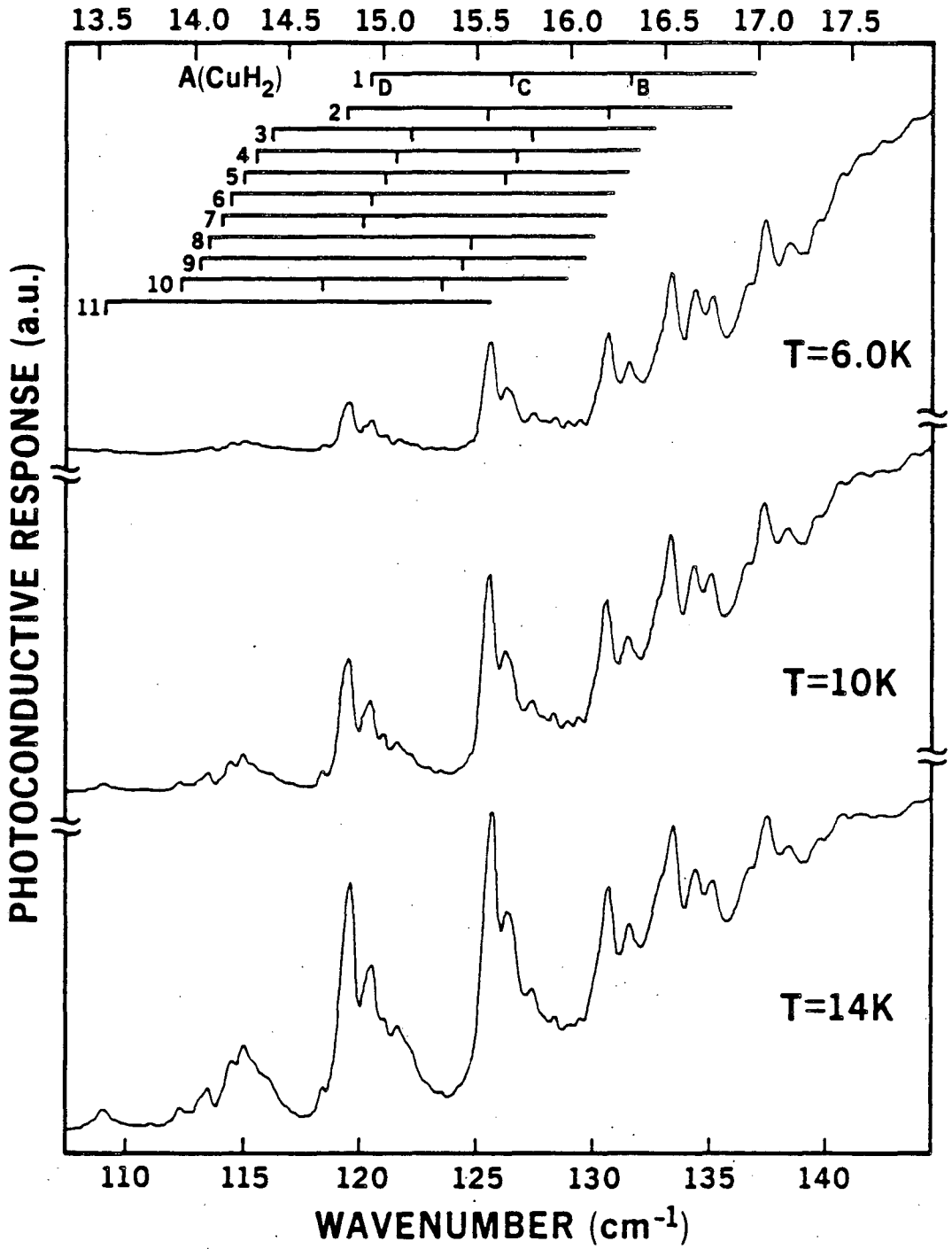
FIGURE CAPTIONS

FIG. 1: Photothermal ionization spectra of the acceptor $A(CuH_2)$. Because of thermal population of shallower 1s-like states, additional line series appear at higher temperatures.

FIG. 2: 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. 3: Photothermal ionization spectra of copper-dihydrogen acceptors in samples containing different isotopes of hydrogen. (a) Grown in an ambient of H_2 and D_2, containing A(CuHD) and $A(CuD_2)$; (b) exposed to a plasma of H_2 and T_2, containing A(CuHT) and $A(CuT_2)$. Both samples also contain $A(CuH_2)$.

FIG. 4: 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. The two nuclei x and y move among several equivalent interstitial positions.



XBL 863-1158

Fig. 1.

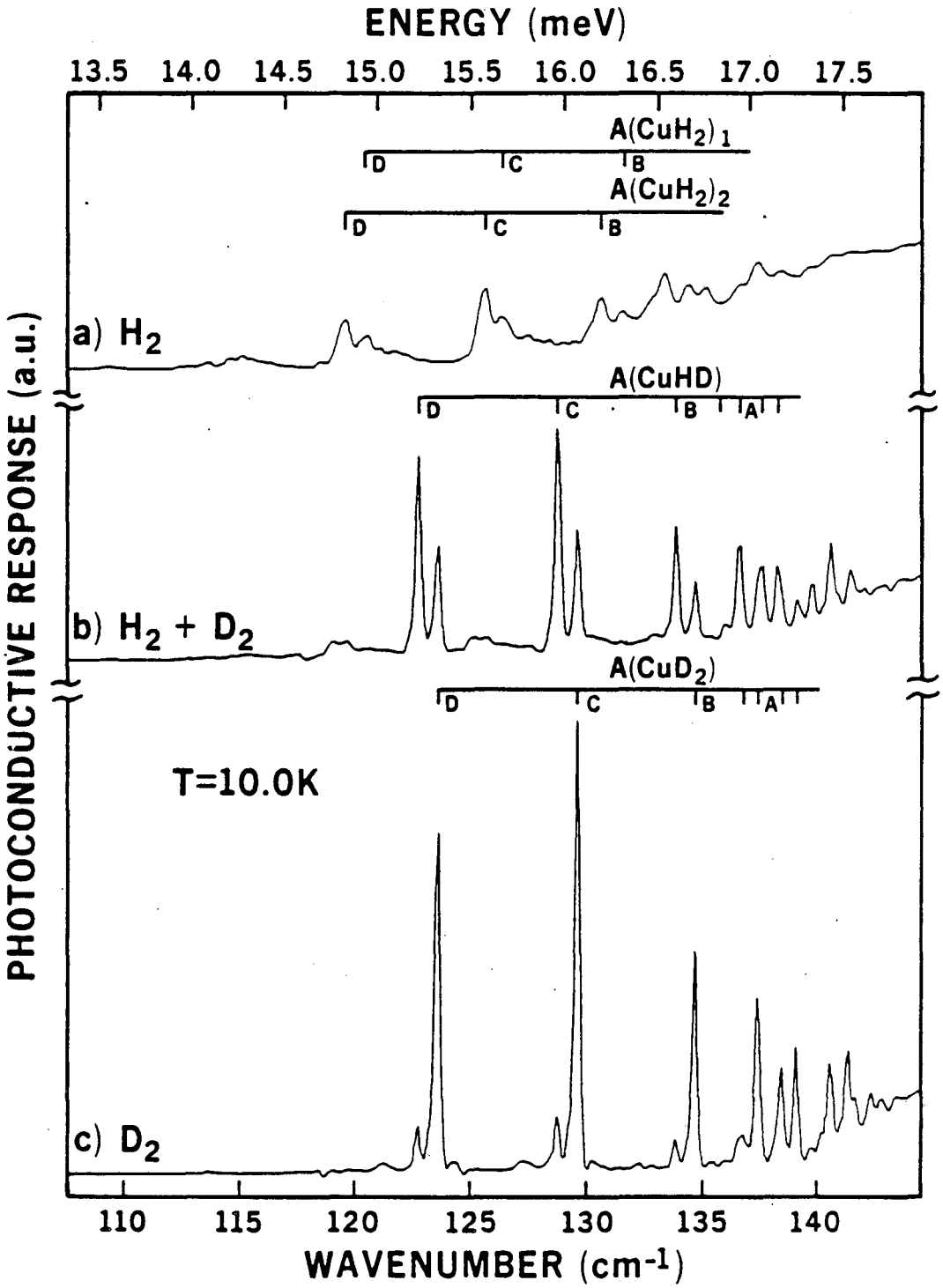


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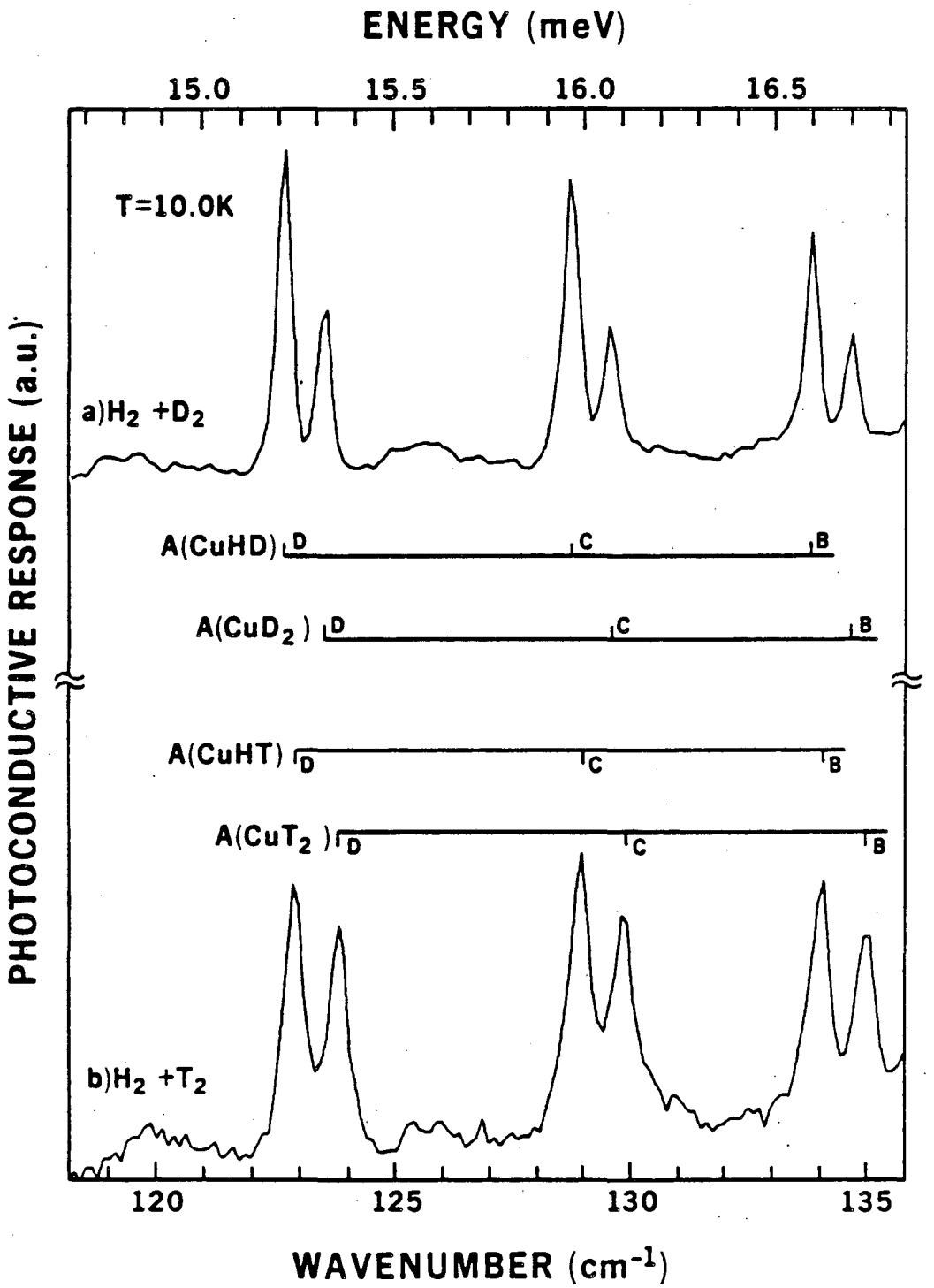
Fig. 2.



XBL 861-39

Fig. 3.

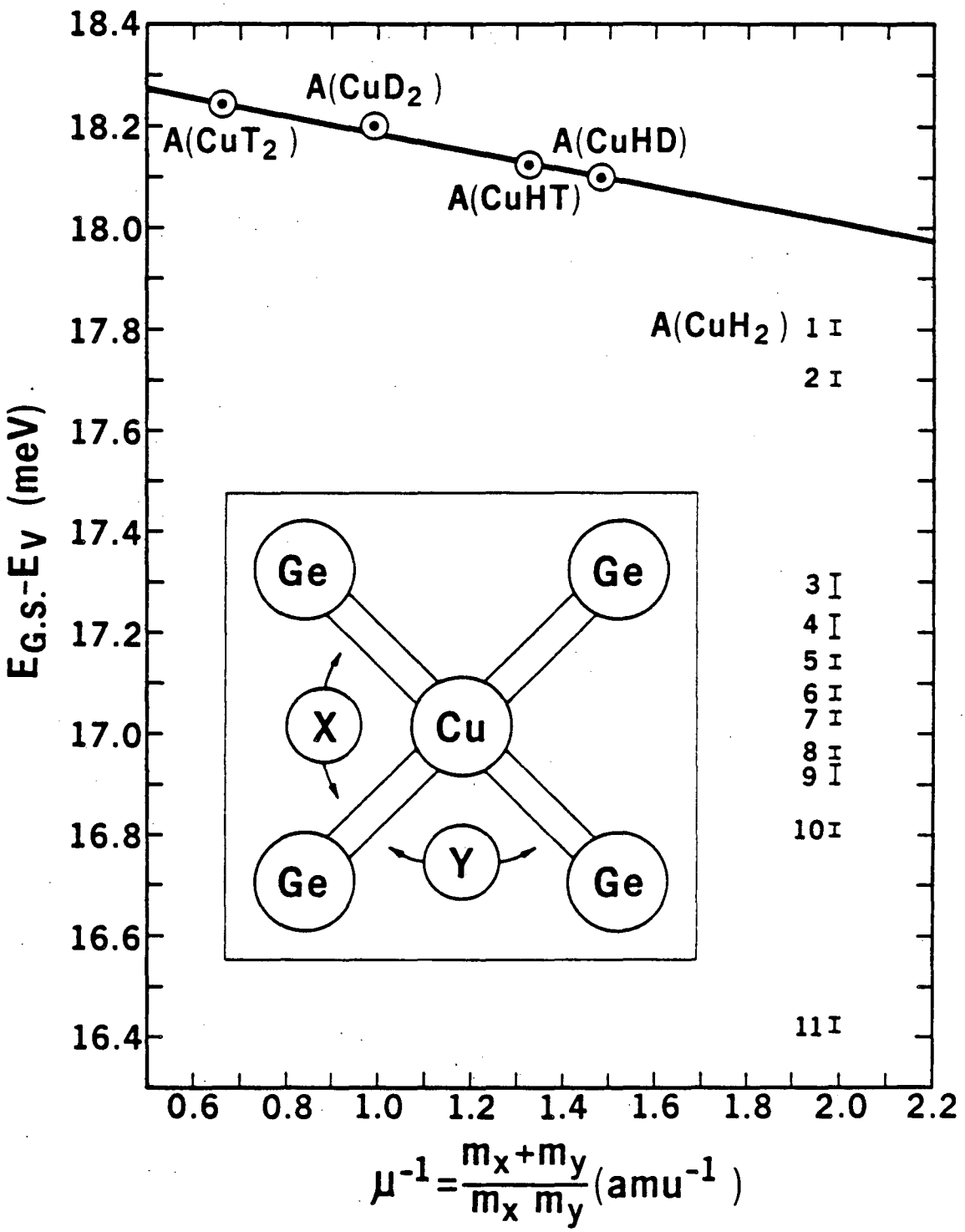


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Fig. 4.

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