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Publication Date
1983-05-01

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May 1983

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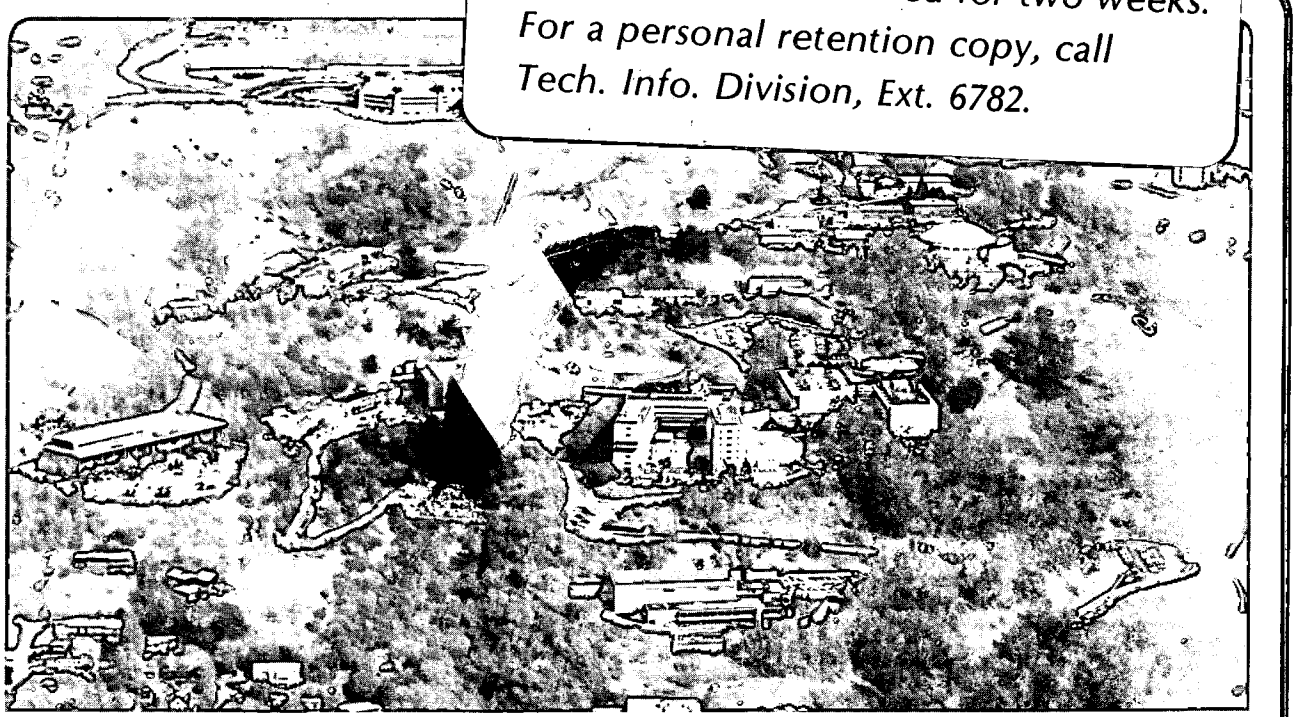

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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*This work was supported in part by the Director's Office of Energy Research, Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and in part by the U.S. National Science Foundation under Contract No. DMR-8203430.

QUENCHED-IN DEEP ACCEPTORS IN GERMANIUM

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Abstract

Quenching from temperatures in the range 500 - 750°C of high purity p-type germanium induces a deep hole trapping state at E_V + 0.23 eV. This level is also seen in γ-irradiated samples from the same material, and is tentatively identified as an oxygen-vacancy complex. Quenching from 700°C of copper-doped germanium induces the normal Cu^-, Cu^{2-} and Cu-H levels, as well as a deep hole trap at E_V + 0.41 eV. Field assisted emission measurements are consistent with this level being due to triply ionized copper.

The nature of shallow level acceptor and donor defects induced in high purity germanium by rapid quenching from around 400°C has been established for many cases (Haller et al 1981). These centers generally include hydrogen in a complex with a heavier substitutional impurity, such as silicon, oxygen or carbon. Much less is understood, however, about the deep defect states induced by thermal treatment. Contamination by the rapidly diffusing copper is always a problem in germanium at elevated temperatures (Logan 1955, Tweet 1956), and the concentration ratio of quenched-in deep levels to shallow levels is always low. Tavendale and Pearton (1983) have recently shown that oxygen plays a major role in the deep levels created in high purity germanium quenched from 875°C. In the present study we have quenched germanium grown under a wide variety of conditions from temperatures in the range of 500 - 750°C, and observed the deep levels induced, using deep level transient spectroscopy (DLTS) (Lang 1974). As well, we have used the field dependent emission from these levels in p-type material to establish their acceptor nature, and have unambiguously identified a previously observed but never identified level in copper-doped p-type germanium as being due to the Cu^{3-} state.

The high purity p-type material ($N_A - N_D = 3 \times 10^{10} - 2 \times 10^{11}$ cm^{-3}) used was grown by the Czochralski technique under a variety of conditions. The ambient during crystal growth was either H_2, N_2 or vacuum, whilst the crucible material was either silica or pyrocarbon-coated silica. The various combinations of gas ambient and crucible material give varying amounts of the four common electrically inactive contaminants in germanium, namely oxygen, hydrogen, silicon, and carbon, enabling correlations with the concentrations of defects induced

by heat treatment. Sections from a gallium-doped crystal ($N_A - N_D$ = 2×10^{15} cm^{-3}) were doped with copper by plating and diffusing at 600°C to achieve a uniform copper distribution. All samples (high purity and doped) were cut into 3 x 3 x 1.5 mm^3 sections, and heated to 500 - 750°C for 15 min on a silica platform within a resistively heated furnace, under an argon atmosphere. Prior to the heat treatment, the samples, the high-purity silicon substrate on which they were mounted, and the quartz tube of the furnace were all cleaned in a mixture $4H_2O$:1HCl; $1H_2O_2$ to minimize copper contamination. Quenching to room temperature was achieved in either of two ways: by withdrawing the platform, and dropping the samples into ethylene glycol, or simply allowing the sections to cool to ambient temperature by dropping them onto an asbestos plate. The former method produced a quench time of < 2 sec, whilst the latter method required ~ 20 sec for the samples to cool to room temperature. After lapping and etching, n^+ contacts were formed to the high purity samples by a short low temperature lithium diffusion (5 min, 250°C), whilst a palladium evaporation to the reverse face provided an ohmic contact. The copper-doped sample had previously had thin, stable n^+ contacts formed prior to quenching by the diffusion of antimony (1 hour, 600°C) from a vapor source. A palladium evaporation after quenching and cleaning formed ohmic contacts to these samples also. The DLTS measurements were performed in the usual manner (Lang, 1974) in a system based on an electronic correlator (Miller et al 1975) and a 1 MHz Boonton 72 B* capacitance meter.

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Quenching the high purity material from any temperature in the range 500 - 750°C into ethylene glycol produced no evident induced deep levels, but rather quenched-in shallow levels at a density of ~ 10^{13} cm^{-3}(500°C) to ~ 10^{15} cm^{-3} (750°C), as determined by 1 MHz C-V measurements on the diode structures. In some instances trace amounts of copper contamination were observed, but this was readily identified by the copper-related DLTS peaks. However, high-purity samples given the slower quench displayed always one (and occasionally two) deep hole traps with levels at E_V + 0.23 eV and E_V + 0.38 eV, respectively. These have previously been correlated with the presence of oxygen and lattice vacancies (Pearton and Tavendale 1982; Pearton et al 1983). Figure 1(a) shows the increasing concentrations of the E_V + 0.23 eV level in samples from the same section as a function of increasing temperature from which the sample was quenched. Figure 1(b) shows the relative concentration of the E_V + 0.23 eV level in samples "slowly" quenched from 750°C as a function of the growth conditions of the parent crystal. The growth ambient (H_2, N_2 or vacuum) made much less difference in the concentration of the level than the crucible material, confirming the results of γ-radiation damage experiments, which correlated a higher concentration of oxygen in the crystal with higher concentrations of the E_V + 0.23 eV level (Pearton et al 1983). However, in the quenching experiments, the E_V + 0.23 eV and E_V + 0.38 eV levels did not always appear together and at the same concentration, meaning possibly that they are not simply two charge states of the same defect as previously thought, but may be related to different forms of oxygen present after the heat treatment.

In the copper-doped material no previously unobserved copper-related levels were oberved after quenching into ethylene glycol (slower quenching allows precipitation of the copper). However, a deep hole trap whose DLTS peak is occasionally observed on the high temperature side of the Cu^{2-} peak in high purity material was much more evident in these samples. This peak has never previously been identified. We measured the activation energy of the level (at zero field) as E_v + 0.41 eV, which correlates closely with the energy level of the Cu^{3-} state observed by Hall effect in compensated material (E_c - 0.26 eV) (Woodbury and Tyler 1957). To clearly identify this level we performed DLTS field-enhanced hole detrapping measurements by varying the electric field strength within the junction diode samples. At constant reverse bias the filling bias pulse amplitude was reduced, allowing us to observe lower field regions within the depletion region. At high enough fields, the Coulombic barrier to emission of a trapped hole is reduced, and the defect state shows a higher emission rate at constant temperature. This is observed on a DLTS spectrum by noting a shift in peak position as the field strength is altered (Kimerling and Benton 1981). This Poole-Frenkel effect (Frenkel 1938, Hartke 1968) leads to an emission rate that is both temperature and field dependent. Thus, the usual detailed balance relation:

$$e_p\ (T) = kT^2 \exp\ (E_t/kT) \qquad (1)$$

becomes

$$e_p\ (E,T) = e_p(T) \exp\ (\Delta E/kT) \qquad (2)$$

where $\Delta E = q(qE/\pi\epsilon)^{1/2}$ is the barrier lowering by the applied field.

For a singly ionized impurity in Ge, $\Delta E = 1.9 \times 10^{-4} qE^{1/2}$. However, the effects of tunneling and correction for the three-dimensional nature of the defect potential will lower this by approximately a factor of two. Since ΔE depends on the charge of the negative ion that has detrapped a hole, we may use this method to identify the charge state of the copper ions giving rise to the various DLTS peaks.

Figure 2 shows the temperature shift of the Cu^-, Cu^{2-}, and the postulated Cu^{3-} (level A) peaks as a function of the reverse bias pulse, at constant reverse bias. From equation (2) we calculate the lowered barrier from the temperature shift at constant emission rate ($e = 100\ s^{-1}$), as a function of the average electric field within the sampled fraction of the depletion region of the diode. Figure 3 shows the measurements obtained for Cu^-, Cu^{2-}, and level A. The slopes of the lines yield:

$$\Delta E = 1.4 \times 10^{-4} qE^{1/2} \text{ for } Cu^-$$
$$= 2.0 \times 10^{-4} qE^{1/2} \text{ for } Cu^{2-}$$
$$= 2.4 \times 10^{-4} qE^{1/2} \text{ for level A}$$

i.e. the barrier lowering scales as the square root of the charge on the negative ion as predicted by the Poole-Frenkel model. The close agreement for level A with that expected for a triply ionized core ion strongly supports our identification as that of Cu^{3-}. We propose that this method may be useful in determining the charge states of many other deep levels in semiconductors. The observation of a Poole-Frenkel effect also confirms the acceptor nature of the copper centers. Due to the much lower field attained in the high purity samples we were unable to get accurate data for the $E_v + 0.23$ eV level, but did

observe a field-induced shift in peak temperature, indicating that this center is also an acceptor, and not a donor which traps holes.

In conclusion, we observed no deep levels in high-purity germanium quenched into ethylene glycol from 500 - 750°C, but slower quenched samples displayed levels correlated with oxygen-vacancy complexes. In quenched, copper-doped germanium we demonstrated the Poole-Frenkel effect in deep levels in germanium for the first time, and used this to clearly identify the charge state of copper giving rise to the various levels.

This work was supported in part by the Director's Office of Energy Research, Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and in part by the U.S. National Science Foundation under Contract No. DMR-8203430.

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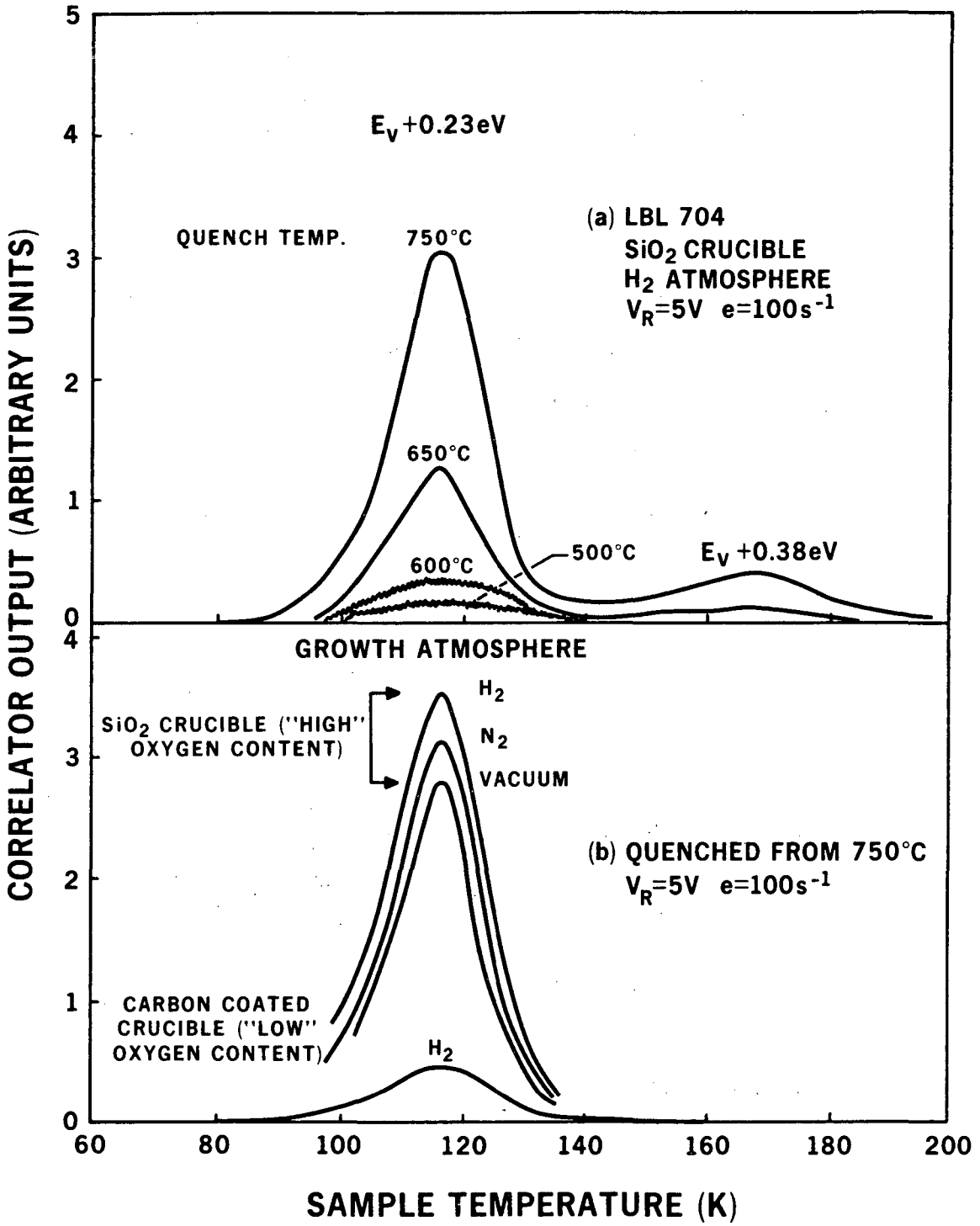
Figure Captions

1. a) DLTS spectra recorded at reverse bias 5V and correlator time constant 10 ms (emission rate e = 100 s^{-1}) for samples of high-purity germanium quenched from temperatures in the range 500 - 750°C. Increasing the quench temperature increases the concentration of the deep acceptor (E_v + 0.23 eV) induced. b) DLTS spectra from samples taken from various crystals, and quenched from 750°C. The crystal growth gas ambient makes much less difference than the crucible material used in the Czochralski growth--this is evidence that oxygen content of the crystals determines the density of E_v + 0.23 eV levels produced by the quench.
2. DLTS spectrum of quenched copper doped germanium samples. For constant reverse bias (5v), the bias pulse amplitude is progressively reduced, lowering the average field strength in the sampled region of the depletion volume. The shift is due to the Poole-Frenkel effect (field-enhanced hole emission).
3. Observed Coulombic barrier lowering for Cu^-, Cu^{2-}, and level A impurities as a function of the average electric field in the junction. The slope of the line is equal to the Poole-Frenkel constant for germanium, for the different charge states on the negative ion remaining after hole emission.



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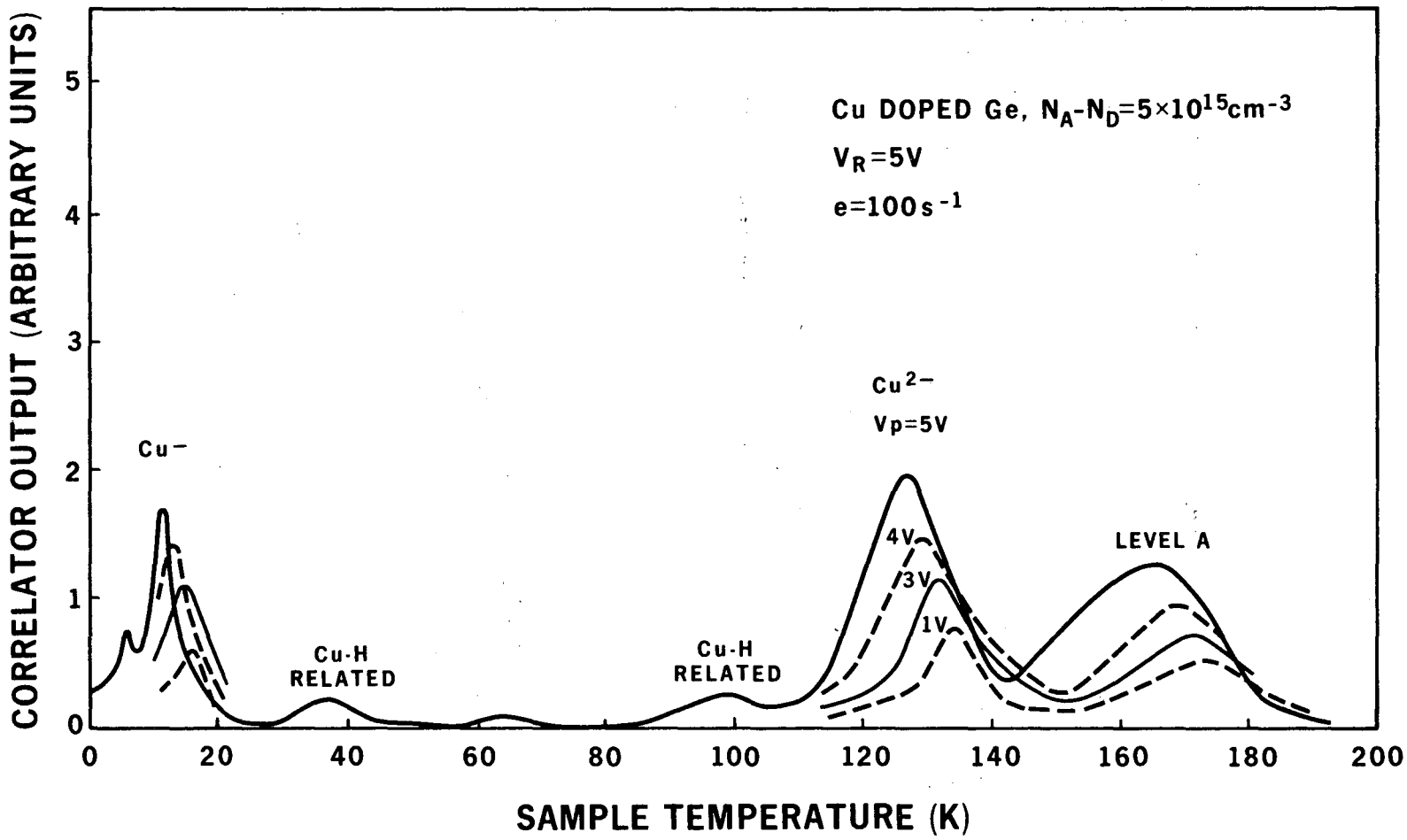

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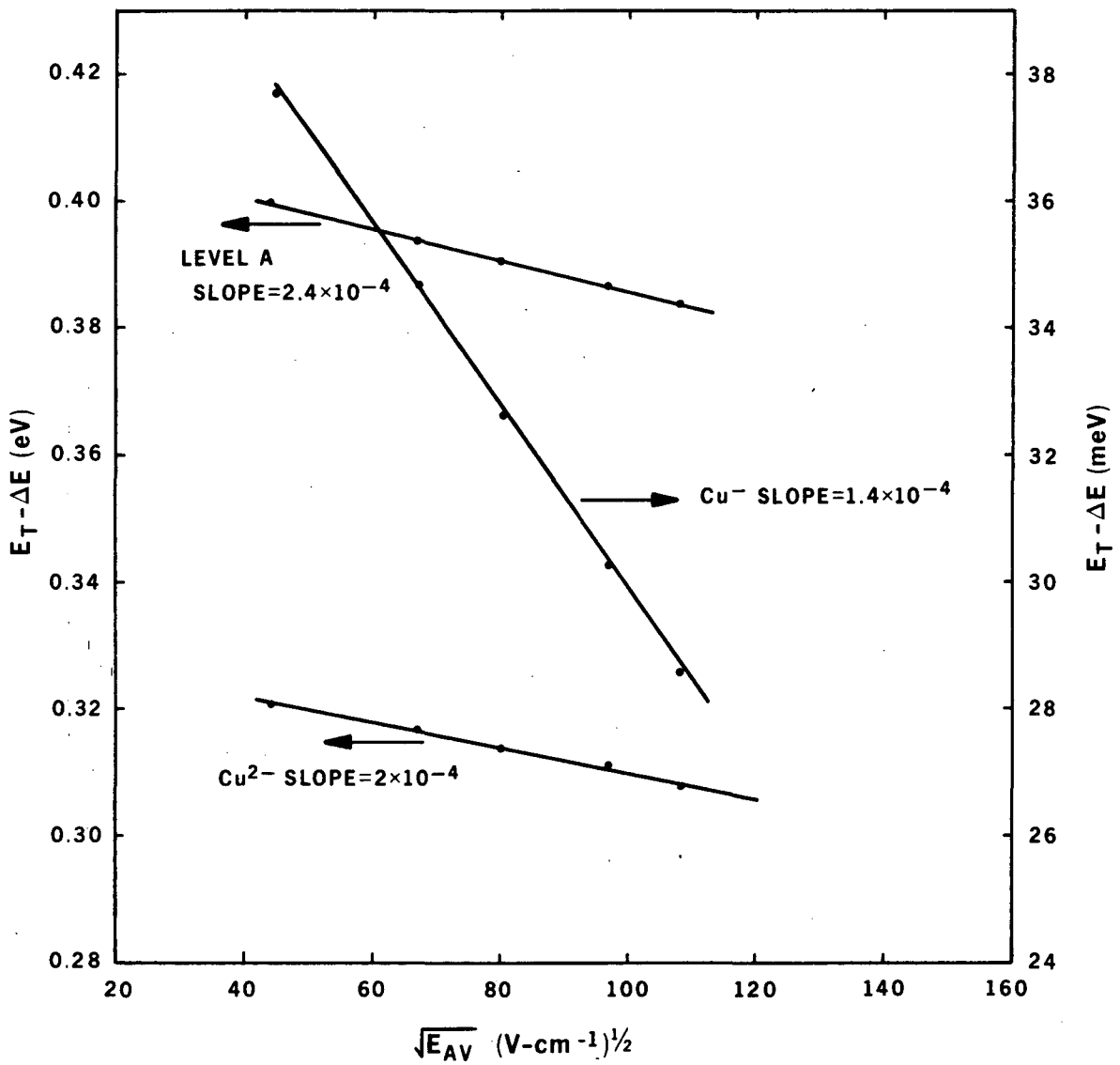

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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