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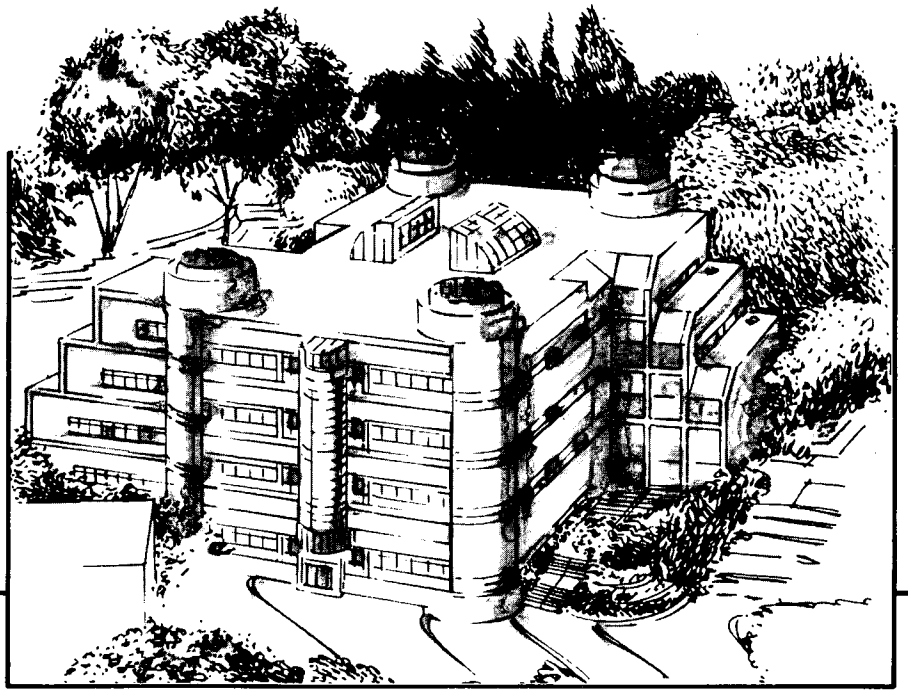

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PHYSICS WITH CHEMICALLY AND ISOTOPICALLY PURE SEMICONDUCTORS

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PHYSICS WITH CHEMICALLY AND ISOTOPICALLY PURE SEMICONDUCTORS

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Abstract

Chemically and isotopically pure semiconductors offer a wealth of interesting physics. We review a number of impurity complexes which were discovered in ultra-pure Germanium. They have led the way to the widely pursued studies of hydrogen in numerous semiconductors. Isotope related effects and processes include neutron transmutation doping, a technique used for a number of silicon and germanium devices. Isotopically pure and deliberately mixed crystals of germanium have been grown recently and have been used to study the dependence of the indirect bandgap and phonon properties on the mass and mass disorder of the nuclei. The large number of stable isotopes of the various semiconductors present a great potential for basic and applied studies. Semiconductor isotope engineering may become a reality because of the new economic and political world order.

PACS Index Numbers: 71.55.-i, 63.20.-e, 66.30.-h, 28.60.+s

I. INTRODUCTION

Purification of semiconductors has remained a primary challenge from the early days of experimentation to today's sophisticated research and application of semiconductors in a wide variety of devices. If one wants to understand or make use of the immense diversity of properties of the many known semiconductors through the introduction of dopant impurities and/or native defects, one preferably starts with materials which are sufficiently pure for the given task.

Perhaps the biggest challenge for the purification of semiconductors has come from the application of silicon and germanium in large volume p-i-n junctions used for the detection and measurement of ionizing radiation [1]. In order to obtain fully depleted detectors with volumes of tens to hundreds of cm^3 at bias voltages of up to a few thousand volts, one has to synthesize crystals with net-dopant concentrations in the 10^{10} to 10^{11} cm^{-3} range.

Since only the difference between the acceptor and the donor concentrations needs to be small in this particular application, one might be led to believe that this is less of a challenge than reading absolute impurity concentrations of this order of magnitude. Indeed, there exists a process which allows very precise compensation of acceptors by mobile, interstitial lithium donors. This so-called "lithium drift" process has been used for over ten years in the production of large volume Si and Ge radiation detectors [2,3]. Because of severe room temperature instability problems with Ge(Li) detectors, a large and ultimately successful effort was launched in the 1970s to develop ultra-pure Ge with purities in the low 10^{10} cm^{-3} [4,5].

It is instructive to realize that at such purity levels we deal with one electrically active impurity for every 10^{12} semiconductor atoms! If net-impurity concentrations of this order of magnitude must be achieved throughout large crystal volumes, it is mandatory that the individual, absolute impurity concentrations are of the same

magnitude. It is simply not possible to grow large crystals with close to perfect compensation extending over large volumes.

Semiconductor physics has been of significant help on the difficult and long path to such extremely pure materials but at the same time it has also profited through the discovery of a large number of impurity and defect complexes which have unique and interesting properties [6]. Much of what we have learned from the development and the study of ultra-pure crystals has or may become useful in some form for doped crystals.

A good example for this kind of knowledge transfer has been the study of hydrogen in semiconductors. The first electronic effects of hydrogen in semiconductors were discovered during the development of ultra-pure germanium [7,8,9]. Both passivation of multilevel acceptors [10,11] and activation of neutral impurities manifest themselves in ultra-pure germanium. In the early 1980s this knowledge was transferred to silicon and led to the discovery of the effective passivation of acceptors and donors [12]. Today the study of hydrogen in practically all elemental and compound semiconductors is pursued worldwide [13,14].

We can expand the concept of purity to include both **chemical** and **isotopic** purity. The latter starts to attract attention because sizable quantities of isotopically pure semiconductor materials have become available through the opening of markets in the former Soviet Union. The international high energy physics collaboration for the determination of the neutrino mass through the study of double beta decay in the isotope ^{76}Ge required several tens of kilograms of this highly enriched isotope in the form of ultra-pure single crystals [15]. These crystals were made into large volume coaxial p-i-n diodes which can detect any internal decays with very high efficiency.

Smaller quantities of isotopically pure and deliberately mixed Ge crystals have been grown [16] and used for a variety of studies. These studies address the dependence of the bandgap on isotope mass [17,18], the properties of phonons in isotopically pure and deliberately mixed crystals [19,20,21], the local vibrational modes of impurities in

isotopically engineered crystals [22], the conduction of heat [23], and the properties of the chalcogenide double donor Se in Ge.

An interesting experiment on the diffusion of Ga in GaAs was recently conducted using the stable isotopes ^{69}Ga and ^{71}Ga [24]. Plans exist to grow isotope superlattices of isotopically enriched and ultra-pure Ge [25]. Such superlattices can be doped after they have been grown by the Neutron Transmutation Doping (NTD) process. The separation of the crystal growth process from doping will allow the formation of interesting superlattices which can be doped sequentially several times to ever higher levels [26].

In this paper we will first review briefly the major findings from the studies of ultra-pure Ge, continue with a discussion of some applications of "purely doped" crystals and finally present recent and future experiments with isotopically pure semiconductors.

II. IMPURITY COMPLEXES IN ULTRA-PURE GERMANIUM

The purification and growth of large volume Ge single crystals with residual impurity concentrations in the 10^{10} cm^{-3} range posed some interesting challenges in regard to the choice of materials (crucibles, ambient gasses, crystal puller envelope, etc.) which would be suitable for such an endeavor, as well as to the choice of characterization techniques which would offer sufficient sensitivity and selectivity. The successful purification and crystal growth techniques have been reviewed in detail [5,6] and we will concentrate here on the unusual aspects of the residual impurities. We recall that practically all high quality ultra-pure Ge is grown in a pure hydrogen atmosphere of ambient pressure from a melt contained in a pure silica crucible. The crystals contain hydrogen and oxygen at concentrations of ~10^{14} cm^{-3}. Both impurities reside electrically inactive in the crystal. Hall [27] discovered that upon heating ultra-pure Ge to temperatures around 400°C followed by rapid quenching, a shallow acceptor at a concentration of ~10^{11} cm^{-3} was formed. The acceptor is not stable at room temperature and transforms into a shallow donor. The donor can be annealed away at temperatures

slightly above 100°C. Using photothermal ionization spectroscopy discovered by Lifshitz and Nad [28], we analyzed these rapid quenching acceptors and donors and found that both had rather unusual properties. Substitution of hydrogen with deuterium induced a measurable shift in the ground state energies of the acceptor and the donor [29]. This was the first direct proof of the presence of hydrogen in these novel centers.

The acceptor was the first one in a semiconductor with a degenerate valence band top which exhibited a split 1s ground state manifold. The ground-state splitting and the isotope shift were found to be caused by the reduced symmetry and an axial strain field of the hydrogen-silicon impurity complex [30]. The hydrogen "activates" a neutral silicon atom to become a shallow acceptor A(H,Si). In crystals grown from graphite crucibles we found an analogous carbon-hydrogen acceptor A(H,C). Theoretical calculations are in agreement with these assignments [31]. Because the 1s ground-state components of A(H,Si) and A(H,C) are, unlike normal acceptors, insensitive to mechanical stress, one can expect very sharp ground-state to bound excited state transitions. Indeed, the sharpest 1s ground-state to bound excited state electronic transitions have been recorded with A(D,C) (D stands for deuterium) acceptors in ultra-pure Ge (Fig. 1).

In the meantime, a wealth of spectroscopy studies using external perturbations such as stress and magnetic fields have been performed on these centers [6,30,32-35]. Further discoveries were made with multivalent acceptors and hydrogen in germanium and silicon. The double acceptors Be and Zn form shallow acceptors in Ge upon binding one hydrogen atom [10,36]. In Si the Be-H acceptor has been shown to be a tunneling hydrogen center [37,38,39]. Theoretical calculations support a structure with the hydrogen atom in local energy minima along the six equivalent [100] directions [31]. The original tunneling model which was based on hydrogen residing in four equivalent sites along the [111] directions was successfully modified for the Be-H center in Si [40].

The center with the richest spectrum of hydrogen related effects is the substitutional triple acceptor Cu in Ge. Isotope shifts in the acceptor ground-state using crystals doped

with H, with D and with both H and D established the presence of two hydrogen atoms in this A(Cu,H_2) center [11] (Fig. 2). The spectroscopic studies were expanded to include tritium. The key finding was that with two hydrogen atoms bound to copper a complicated ground-state manifold resulted from the nuclear motion of the protons. Substitution of one or both hydrogen atoms with deuterium or tritium led to a freezing of the nuclear motion accompanied by the reduction of the electronic ground-state multiplet to a single level. The Devonshire model of the hindered rotor proved to give a quantitative description of the properties of the A(Cu,H_2) centers [41].

Summarizing this section on ultra-pure Ge we can state that only the great purity made possible the discovery and the successful identification of a number of hydrogen containing centers. Both activation of neutral impurities and partial and full passivation of multivalent acceptors was established. These studies led directly to the hydrogen passivation studies which are still conducted with numerous semiconductors today [13].

III. ISOTOPE EFFECTS IN SEMICONDUCTORS

With very few exceptions most semiconductor research and technology is completely oblivious to the existence of stable semiconductor isotopes. This is quite understandable for several reasons. First, it has been very costly to obtain even the smallest quantities of isotopically enriched semiconductor materials. Second, most effects caused by differences in isotope nuclear masses are small and therefore only of interest for specific basic studies.

1. Neutron Transmutation Doping (NTD)

Transmutation of stable semiconductor isotopes into different elements acting as dopants following thermal neutron capture has made use of specific isotopes for some time. The technologically most important case is doping of ultra-pure Si with thermal neutrons. The resulting homogeneity of the phosphorus donor concentration is used in

the fabrication of the majority of high voltage, high power silicon controlled rectifiers (SCRs) [42,43]. The neutron transmutation doping process in silicon is based on the following reaction:

$$ {}^{30}_{14}\mathrm{Si} + \mathrm{n} \rightarrow {}^{31}_{14}\mathrm{Si} \xrightarrow[T_{1/2} = 2.6\ \mathrm{hrs}]{\beta^-} {}^{31}_{15}\mathrm{P} + e^- + \bar{\nu}_e \qquad (1) $$

The other isotopes are ^{28}Si (92.23%) and ^{29}Si (4.61%). Only 3.10% of natural silicon is ${}^{30}_{14}$Si. The maximum phosphorus concentration is practically limited to levels around 10^{16} cm^{-3}. This limit is, of course, not a theoretical limit given by the total concentration of ${}^{30}_{14}$Si. It is related to the maximum available flux of thermal neutrons, the radiation damage caused by fast neutrons and to secondary transmutation of P into S, a deep double donor.

Other semiconductors have been successfully doped by NTD. Germanium, which has five stable isotopes becomes p-type. The majority impurities are gallium acceptors created in the decay of ${}^{71}_{32}$Ge. The compensating donors are arsenic created in the decay of ${}^{75}_{32}$Ge. The NTD process has been most successful in the development of very low temperature Ge thermistors which are used in the bolometric detection of very far infrared electromagnetic radiation (1 mm > λ > 250 μm). The widest application of such low temperature sensors is occurring in the field of submillimeter radioastronomy and astrophysics. All the advanced large radio telescopes are currently equipped with bolometer arrays using NTD Ge operated at temperatures between 100 and 300 mK [44].

Fig. 3 shows the logarithm of the resistivity of ten selected NTD Ge crystals as a function of $T^{-1/2}$. Hole conduction occurs via variable range hopping as predicted by Shklovskii's and Efros' theory [45]. Neutron exposure and the resulting acceptor and donor concentrations are given in Table I. What makes NTD attractive is the extremely good dopant uniformity. The very large size of a nuclear reactor compared to the size of a semiconductor crystal guarantees a very homogeneous neutron flux. The absorption cross sections for the usual semiconductor nuclei are relatively small (~10^{-24} cm^{-2})

resulting in minimal self shadowing and, in the case of Ge, the various stable isotopes have been mixed thoroughly since their birth in nucleosynthesis. In order to fully profit from these advantages of NTD one must use ultra-pure semiconductors. Much of the floating zone Si is grown for applications using NTD.

2. *Isotope Superlattices*

The availability of each of the stable Ge isotopes in highly enriched form has led to a proposal to grow isotope superlattices [25]. MBE grown undoped $^{x}Ge:^{y}Ge$ superlattices hold promise for interesting phonon studies. For superlattices with very small numbers of atomic layers of each isotope, one expects a wealth of Brioullin zone folding phenomena [46]. The growth of thicker $^{70}Ge:^{74}Ge$ superlattices followed by NTD allows the formation of very abrupt n-i-p-i superlattices. The interface abruptness in the different isotope layers is expected to be sharper than when growth with dopants is performed. Studies of this kind will allow a quantitative determination of dopant and host atom interdiffusion at the atomic level.

A recent study of this kind in GaAs made use of superlattices consisting of $^{69}_{31}GaAs$ and $^{71}_{31}GaAs$ layers [24]. Arsenic is monoisotopic and does not play a role in this study. Secondary ion mass spectroscopy (SIMS) was used to measure Ga interdiffusion between the individual layers after annealing at 900°C for 10 hrs. (Fig. 4). It is unfortunate that the substrates for these experiments were strongly Si doped and that the Si appears to have caused deviations of the Ga diffusion constant from the equilibrium value in GaAs.

3. *Bulk Properties Depending on Isotopic Composition*

The bandgap of a semiconductor depends very lightly on the isotopic composition of its constituents. Recent photoluminescence experiments by Davies et al. [17,18] used isotopically and chemically pure Ge crystals to determine this dependence. The

introduction of small concentrations of acceptors and donors proved useful in obtaining very accurate data through no-phonon (NP) transitions of impurity bound excitons (Fig. 5). The indirect bandgap E_I is found to move to higher energy with increasing atomic Ge mass A (Fig. 6):

$$dE_I/dA = 0.35 \pm 0.02 \text{ meV} \tag{2}$$

The isotope dependence of the bandgap has two contributions: electron-phonon coupling and the isotope dependence of the lattice constant. From accurate experimental data one can estimate both of these contributions. The lattice constant effect, or volume term, gives $(dE_I/dA)_V = 0.044$ meV. The electron-phonon term is estimated using the known temperature dependence of the bandgap and a simple harmonic oscillator model for the mean-square displacement $\langle u^2 \rangle$ of the atoms. At low temperatures the power expansion of the mean-square displacement leads to $\langle u^2 \rangle \propto 1/\sqrt{A}$, with A = isotope mass. A simple estimate leads to

$$(dE_I/dA)_{e\text{-}ph} = 0.22 \text{ to } 0.30 \text{ meV}. \tag{3}$$

The two contributions add to a value range which is close to the experimentally determined mass dependence. A recent first-principle calculation [47], on the other hand, leads to a slight overestimate $(dE_I/dA)_{e\text{-}ph} = 0.42$ meV. It will be interesting to explore the isotope mass dependence of other conduction band extrema.

The phonon energies $\hbar\omega$ depend most directly on the isotope mass $\hbar\omega \propto 1/\sqrt{A}$. Experimentally this dependence is fully verified.

An interesting question arises when one explores the effects of isotope disorder on the four different types of phonons. Line broadening and shifts in $\hbar\omega$ may be expected. Two groups have reported experimental studies of these effects [20,21]. As expected, the disorder effects were largest in isotope engineered Ge crystals containing equal parts of ^{70}Ge and ^{76}Ge [48].

IV. SUMMARY AND OUTLOOK

We have shown that chemically and isotopically pure semiconductors offer a wealth of interesting physics. The chemical purification has been pushed as far as necessary for most applications and one cannot expect that fundamental semiconductor studies could generate an incentive large enough to strive for even higher purities. One new application of a high purity semiconductor involves the development of ultra-pure liquid phase epitaxy grown GaAs. Epilayers of up to 100 μm with net-donor concentrations N_D–$N_A \simeq 5\times10^{12}$ cm^{-3} and moderate compensation (0.3-0.7) have been grown successfully [49]. GaAs epilayers which have net-impurity concentrations of this order of magnitude may become useful for room temperature X-ray detector applications and low temperature far infrared photoconductor devices. Such pure crystals are expected to exhibit hydrogenic donor spectra with unprecedented resolution. Extreme purity is of great importance for high resolution spectroscopy studies because the Bohr orbits of the ground- and the bound-excited donor states are extremely large (≥ 100 Å), leading to wavefunction overlap and line broadening already at very low impurity concentrations.

Using isotopically controlled superlattices one will be able to make very accurate interdiffusion measurements. NTD may be especially useful with isotopically engineered III-V and II-VI compound and alloy semiconductor systems.

In closing, we would like to draw the attention to Table II which lists but a few of the stable isotopes of elements which are of current interest for semiconductor science and technology. Many more interesting elements which are either a component of a semiconductor or can act as dopants can be found in Ref. [50]. Semiconductor isotope engineering is evolving.

Acknowledgments

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Table I. NTD Ge thermistor data

NTD#	n Dose (cm^{-2})	N_{Ga} (cm^{-3})	N_{As} (cm^{-3})	N_{Se} (cm^{-3})	$N_{Ga} - \Sigma N_D$ (cm^{-3})
4	3.38E+17	9.94E+15	2.83E+15	1.86E+14	6.74E+15
5	7.50E+17	2.21E+16	6.29E+15	4.13E+14	1.50E+16
13	1.24E+18	3.65E+16	1.04E+16	6.83E+14	2.47E+16
15	1.54E+18	4.53E+16	1.29E+16	8.49E+14	3.07E+16
16	2.07E+18	6.09E+16	1.73E+16	1.14E+15	4.13E+16
18	2.61E+18	7.67E+16	2.19E+16	1.44E+15	5.20E+16
26	2.82E+18	8.29E+16	2.36E+16	1.55E+15	5.62E+16
28	3.07E+18	9.03E+16	2.57E+16	1.69E+15	6.11E+16
12	3.33E+18	9.79E+16	2.79E+16	1.83E+15	6.64E+16
25	4.20E+18	1.23E+17	3.52E+16	2.31E+15	8.37E+16

Table II. (All data are from Ref. 50)

Isotope	Abundance (%)	Thermal neutron capture Cross section (10^{-24} cm^2)	Neutron transmutation product
${}^{10}_{5}B$	19.8	3838 (n,α) 0.52	${}^{7}_{3}Li + {}^{4}_{2}He$ ${}^{11}_{5}B$
${}^{11}_{5}B$	80.2	0.005	${}^{12}_{6}C$
${}^{12}_{6}B$	98.89	0.0034	${}^{13}_{6}C$
${}^{13}_{6}C$	1.11	9×10^{-4}	${}^{14}_{7}N$
${}^{14}_{7}N$	99.63	0.076	${}^{15}_{7}N$
${}^{15}_{7}N$	0.37	4×10^{-5}	${}^{16}_{8}O$
${}^{16}_{8}O$	99.76	1.78×10^{-4}	${}^{17}_{8}O$
${}^{17}_{8}O$	0.038	0.235 (n,α)	${}^{14}_{6}C + {}^{4}_{2}He \rightarrow {}^{14}_{7}N$
${}^{18}_{8}O$	0.204	1.58×10^{-4}	${}^{19}_{9}F$
${}^{27}_{13}Al$	100	0.231	${}^{28}_{14}Si$
${}^{28}_{14}Si$	92.23	0.17	${}^{29}_{14}Si$
${}^{29}_{14}Si$	4.67	0.10	${}^{30}_{14}Si$
${}^{30}_{14}Si$	3.10	0.11	${}^{31}_{15}P$
${}^{31}_{15}P$	100	0.18	${}^{32}_{16}S$
${}^{32}_{16}S$	95.02	0.53	${}^{33}_{16}S$
${}^{33}_{16}S$	0.75	0.095 (n,α)	${}^{30}_{14}Si + {}^{4}_{2}He$
${}^{34}_{16}S$	4.21	0.24	${}^{35}_{17}Cl$
${}^{36}_{16}S$	0.017	0.15	${}^{37}_{17}Cl$
${}^{64}_{30}Zn$	48.6	0.78	${}^{65}_{29}Cu$
${}^{66}_{30}Zn$	29.7	1.0	${}^{67}_{30}Zn$
${}^{67}_{30}Zn$	4.1	7.0	${}^{68}_{30}Zn$

$^{68}_{30}Zn$	18.8	0.88	$^{69}_{31}Ga$
$^{70}_{30}Zn$	0.62	0.098	$^{71}_{31}Ga$
$^{69}_{31}Ga$	60.1	1.7	$^{70}_{30}Zn$ (0.2%) $^{70}_{32}Ge$ (99.8%)
$^{71}_{31}Ga$	39.9	4.7	$^{72}_{32}Ge$
$^{70}_{32}Ge$	20.5	3.25	$^{71}_{31}Ga$
$^{72}_{32}Ge$	27.4	1.0	$^{73}_{32}Ge$
$^{73}_{32}Ge$	7.8	15.0	$^{74}_{32}Ge$
$^{74}_{32}Ge$	36.5	0.36	$^{75}_{33}As$
$^{76}_{32}Ge$	7.8	0.16	$^{76}_{34}Se$

FIGURES

Fig. 1 The photothermal ionization spectrum of the shallow carbon-deuterium complex A(D,C) in ultra-pure Ge. The ground-state of A(D,C) is split by 1.98 meV leading to two sets of hydrogenic line series. At T=7.5 K the upper ground-state component is only lightly populated, resulting in relatively weak line intensities ($A(D,C)_1$). The hydrogenic line series of the residual acceptors Al and B are fully resolved. The sample size was ~$(0.5)^3$ and the total acceptor concentration was ~10^{11} cm^{-3}.

Fig. 2 Spectra of the copper-dihydrogen, copper-hydrogen-deuterium and copper-dideuterium complexes in ultra-pure Ge. Spectrum a) of a crystal grown in H_2 shows a broad line due to the tunneling motion of hydrogen in the Cu-H_2 complexes; spectrum c) was recorded with a crystal grown in D_2. It shows only one sharp series of lines because the higher mass of D suppresses tunneling; spectrum b) of a crystal grown in H_2+D_2 shows an additional, third series of lines due to C-H,D acceptor complexes.

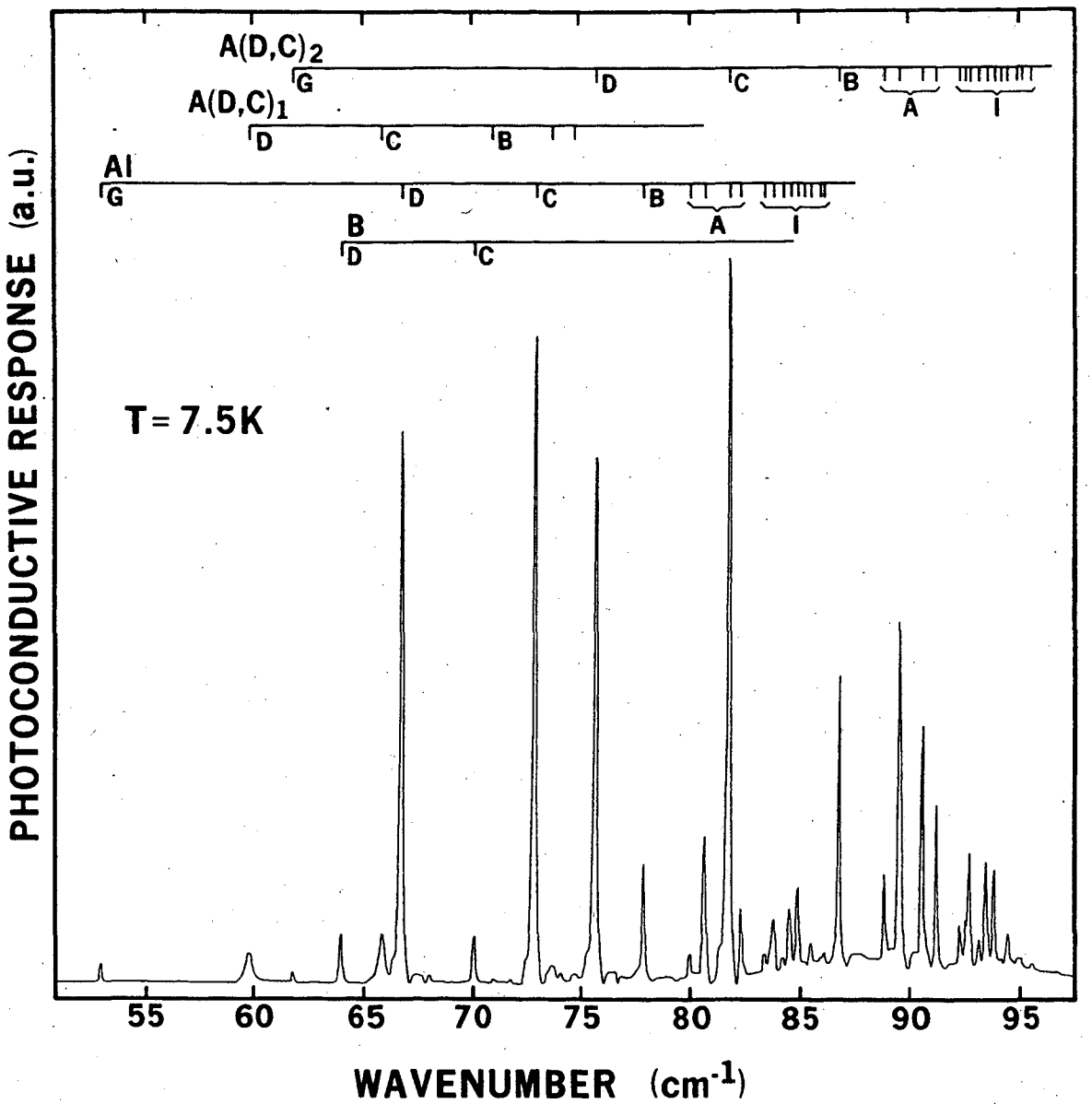
Fig. 3 Logarithm of the resistivity ρ as a function of $T^{-1/2}$ for ten selected NTD Ge crystals. The neutron dose and the resulting dopant concentrations are listed in Table I. (Courtesy J. Beeman, Lawrence Berkeley Laboratory)

Fig. 4 Normalized $^{69}_{31}Ga$ and $^{71}_{31}Ga$ profiles measured by SIMS. (a) An as-grown sample, and (b) a sample annealed at 900°C for 10 hrs. Vertical axes denote relative fractions. (Courtesy Tan *et al.*, Ref. 24)

Fig. 5 Luminescence from the decay of free excitons (FE) and excitons bound to Cu triple acceptors and P donors in ^{70}Ge and ^{74}Ge at 4.2 K. The subscripts indicate the L-point phonons involved in each transition (Courtesy Gordon Davies *et al.*, Ref. 18)

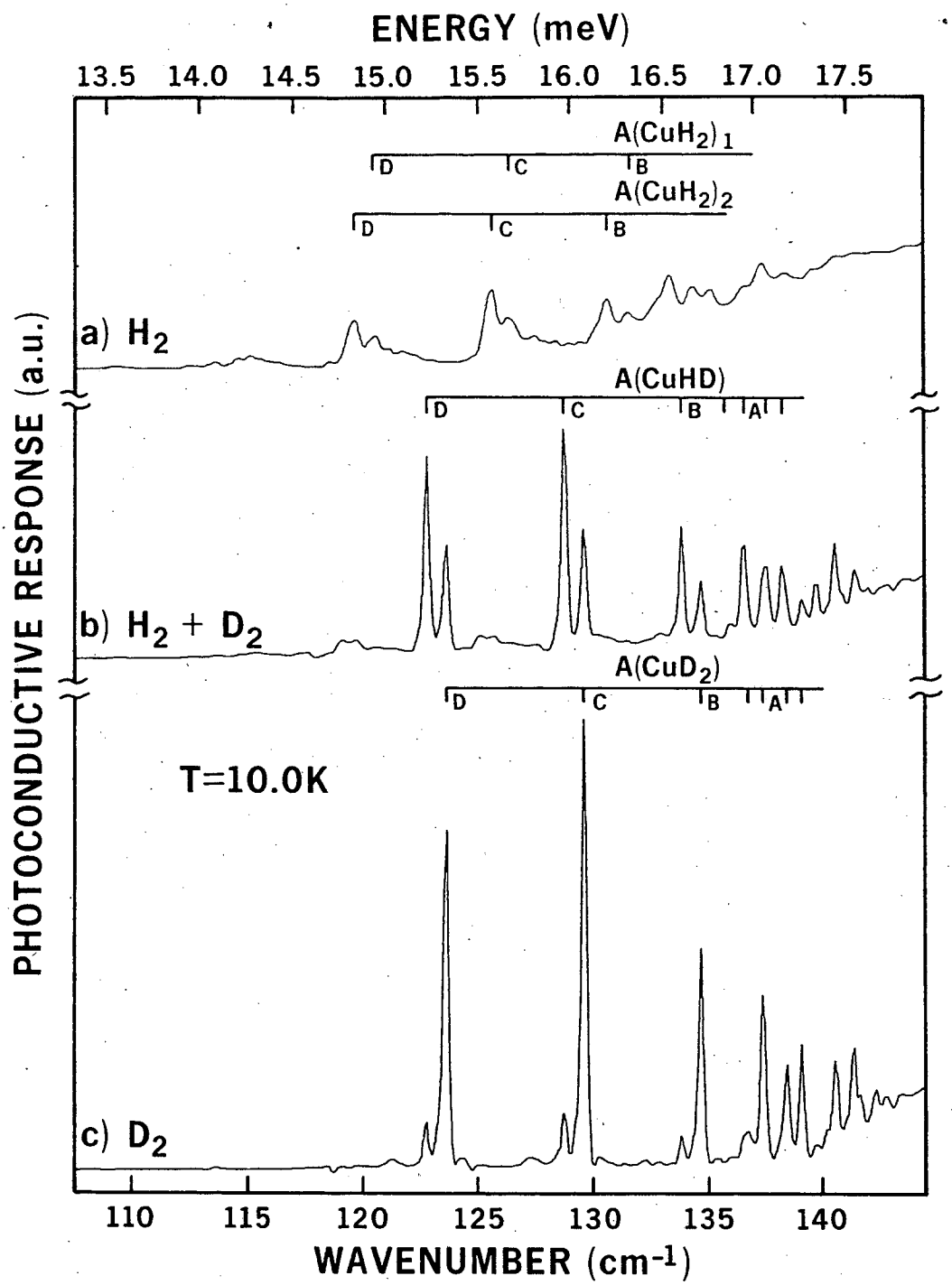
Fig. 6 Exciton no-phonon recombination energies in several isotopically pure and one natural Ge crystal. The P donor and Cu acceptor bound excitons show the same

isotope mass dependence, i.e., the dependence of the bandgap on isotope mass. (Courtesy Gordon Davies *et al.*, Ref. 18)



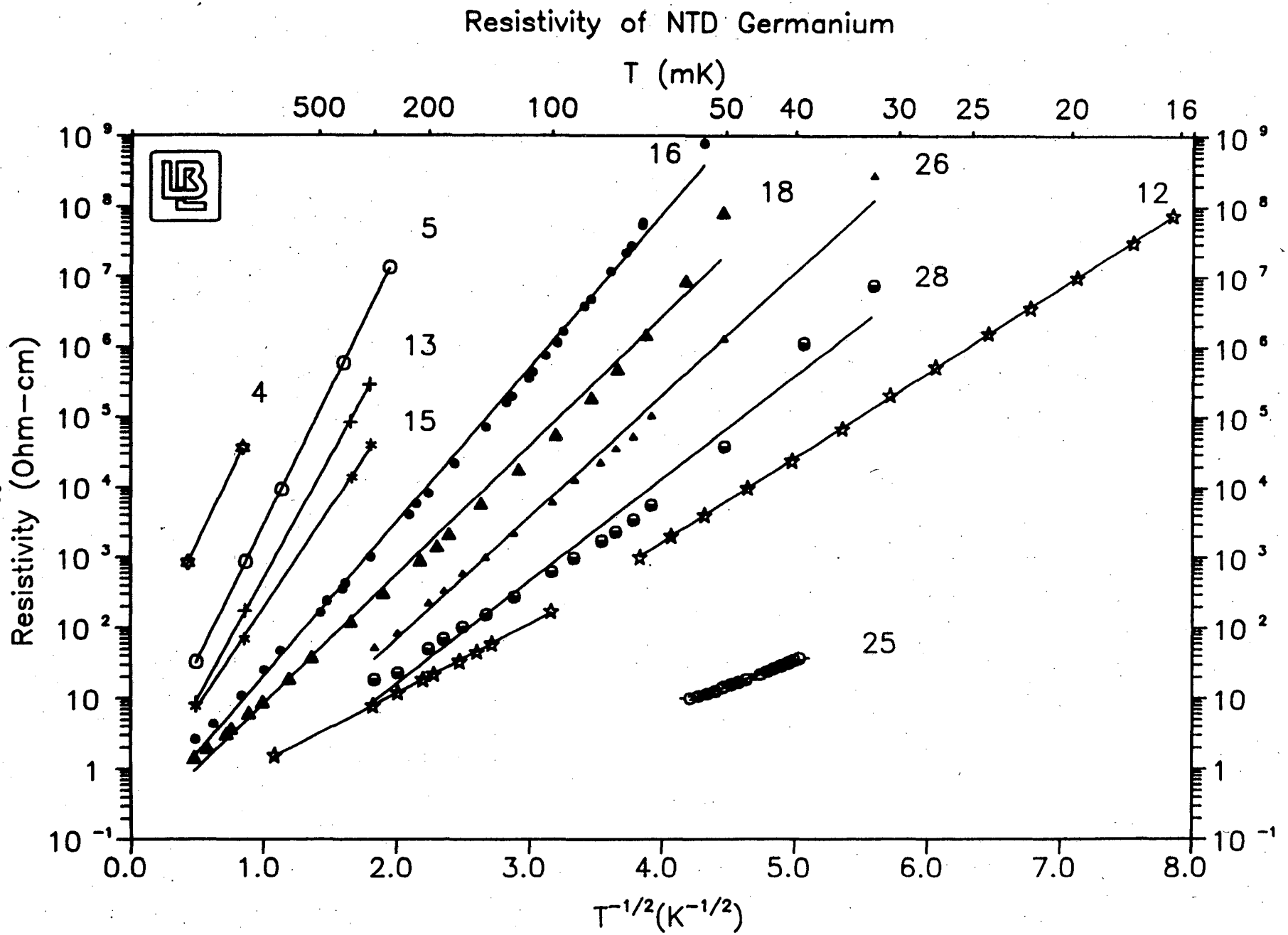
XBL 863-1160

Fig. 1



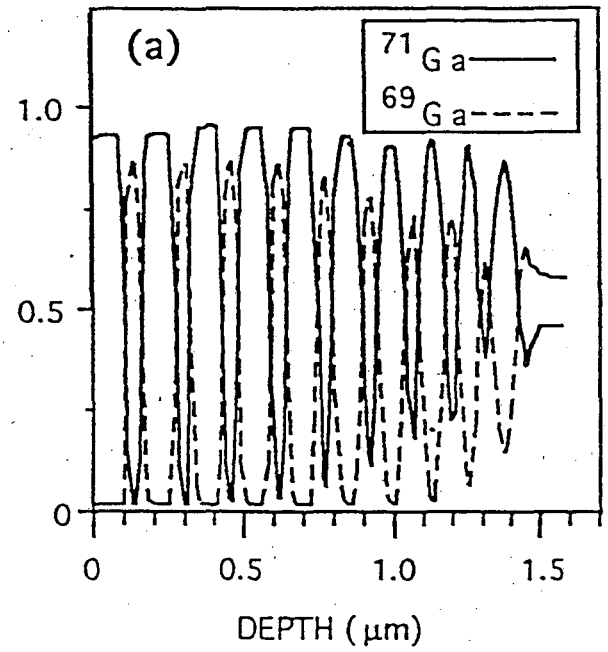
XBL 863-1157

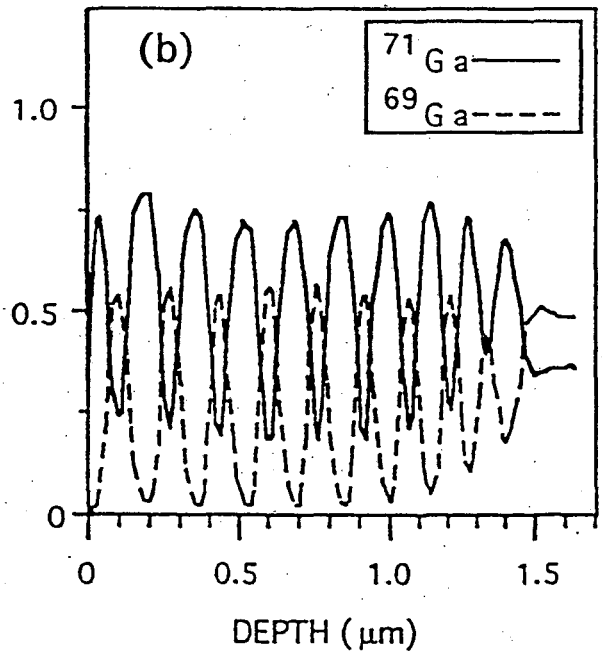
Fig. 2



XBL 935-641

Fig. 3





XBL 935-660

Fig. 4

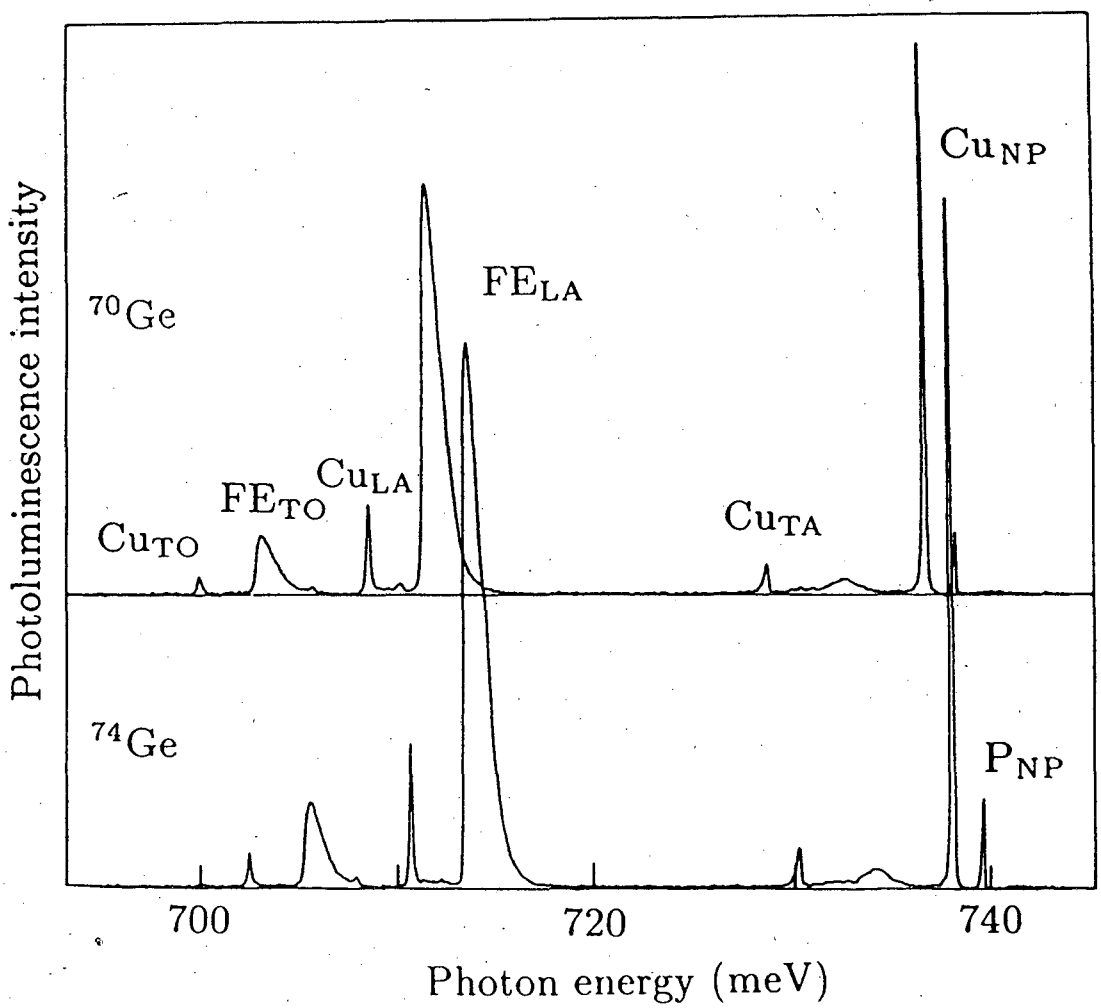


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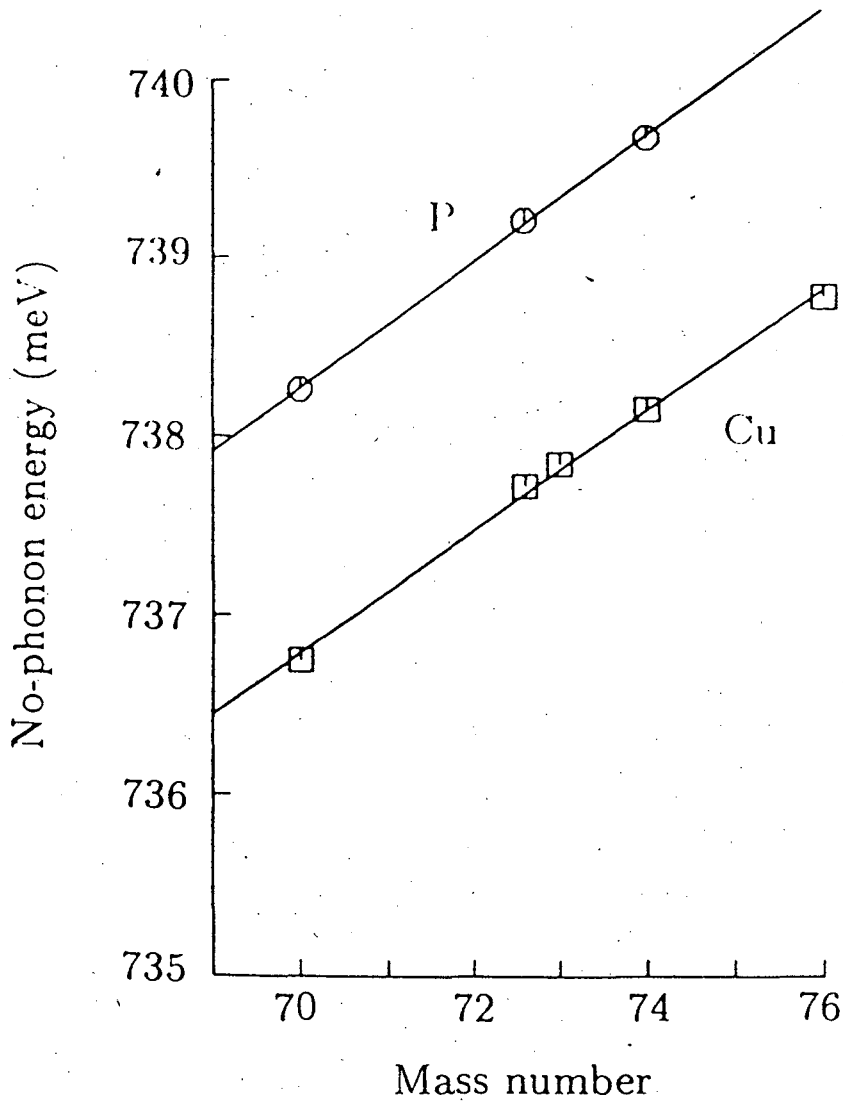
Fig. 5



XBL 935-658

Fig. 6

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