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PHOTOELECTRIC SPECTROSCOPY OF RESIDUAL IMPURITIES IN ULTRA-PURE GERMANIUM AND SILICON

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PHOTOELECTRIC SPECTROSCOPY OF RESIDUAL IMPURITIES
IN ULTRA-PURE GERMANIUM AND SILICON*

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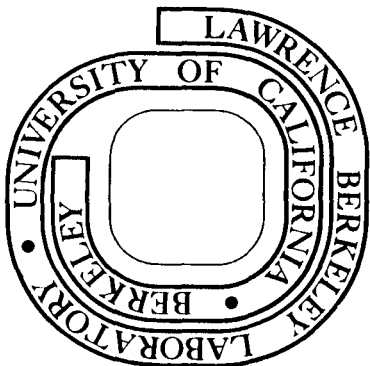
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ABSTRACT

Using photoelectric spectroscopy the residual impurities in a large number of ultra-pure germanium and some silicon single crystals were investigated. Our Far Infrared Spectrometer consists of a Michelson Interferometer with an on-line computer and a helium cryostat with constant temperature option. The instrumental resolution is limited to ~ 0.15 cm^{-1} (= 0.02 meV). With samples of $\sim 1/10$ cm^3 volume and net impurity concentrations of $\sim 10^9$ cm^{-3}, high resolution spectra with signal-to-noise ratios > 100 can be otained in minutes.

Special attention was devoted to the formation of good electrical contacts to the samples since they strongly influence the signal-to-noise ratios. Various techniques using liquid and solid phase epitaxy, ion implantation and metal evaporation were investigated. Using IR spectroscopy together with Hall effect measurements, a systematic investigation of the group III and V impurities and their sources was possible. The dominant impurities in ultra-pure germanium are B, Al and P. The acceptors B and Al do not follow simple segregation behavior in germanium. This may be caused by these elements forming complexes with oxygen and possibly silicon. A number of hitherto undiscovered, hydrogenic acceptors and donors were found; several may be due to impurity-impurity complexes. The general impact of photoelectric spectroscopy on the development of ultra-pure germanium is discussed.

INTRODUCTION

In 1966, R.N. Hall (1966) presented a feasibility study for the fabrication of large germanium single crystals pure enough to produce p-i-n structures with i-region widths in the cm range. It was a challenging task indeed, since net-impurity concentrations in the 2×10^{10} cm^{-3} range were needed. This concentration range was about two orders of magnitude lower than reached at that time.

In early 1971, net-impurity concentrations in the 10^9 to 10^{10} cm^{-3} range over sections several centimeters long of single crystals were reported by at least two laboratories.[+] This development eliminated the need for the lengthy, unpredictable process of lithium drifting for radiation detectors, thereby simplifying their production.

In the last few years, high-purity Ge became available commercially and room temperature storage of detectors, fabrication of detector arrays and telescopes, and many special applications have been developed to the point where high-purity Ge detectors are beginning to displace Li-drifted devices. The availability of high-purity Ge has led to recent discoveries on exciton condensation that have brought Ge back into the solid state physics field.

The purpose of this work is to demonstrate the unique role photoelectric spectroscopy (Lifshits T M and YaNad F 1965; Sidorov V I and Lifshits T M 1967), has played in the development of high-purity Ge, the purest material ever made. The difficulty producing such pure material is illustrated by the fact that only one commercial supplier presently offers a large selection of ultra-pure crystals.[*] At the Lawrence Berkeley Laboratory, we have been involved in high-purity Ge research and development since 1970. Over 400 crystals have been grown and many of them have been used for our own detector needs. At the beginning of our R&D effort, it was not possible to predict what kinds of new phenomena would be encountered. No high-resolution method was available that was sensitive enough to separate the shallow acceptor and donor levels produced by the group IIIA and group VA elements of the periodic system. Low temperature Hall effect measurements gave the impurity concentrations, but the insensitivity of the method to slight energy level differences did not permit determination of

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[*] General Electric Co., Space Technology Products, King of Prussia Park, Philadelphia, PA.

the nature of these residual impurities (Wichner R et al 1974). The
situation was further confused by the non-segregating nature of one of
the dominant shallow acceptors and the excessive trapping of detectors
fabricated from dislocation-free material. Further complications were
evident in Hall's (1975) discovery of so-called "quenched-in" acceptors
and donors during his quenching experiments from temperatures as low as
400° C, though the nature of these levels remained unexplained. Recently,
some progress has been made, thanks to photoelectric spectroscopy. With
this method, "non-classical" phenomena have been discovered and they
will be discussed later.

Secombe and Korn (1972) were the first to apply photoelectric spec-
troscopy to high-purity Ge. They were followed by Bykova E M et al (1973)
and Haller and Hansen (1974) and Skolnick M S et al (1974). The high-
resolution spectra of shallow acceptors has stimulated substantial work on
the theory of hydrogenic levels (Baldereschi A and Lipari N O (1977)).
Photoelectric Spectroscopy has transformed the art of high-purity Ge
purification and crystal growth into a science. The interferometer
and a Fast Fourier Transform Program are essential tools for successful
application of this kind of spectroscopy. The Jaquinot and Fellget advan-
tages improve the signal-to-noise ratio for high resolution spectra of
shallow levels in Ge for a factor of about 100 to 1000 as compared with
classical grating spectrometers (Bell 1972), under otherwise equal exper-
imental conditions.

EXPERIMENTAL

Our main investigations of shallow hydrogenic acceptors in pure Ge
and Si use an interferometer with 7 inch, f=1.5 optics and a maximum
mirror travel of 5 cm. With single-sided interferograms the resolution
is limited to $\Delta\nu=0.1$ cm^{-1}. The light source is a high-pressure mercury
arc lamp. The frequency range can be changed with a selection of Mylar
beam splitters and Yoshinaga filters (Yamada Y et al 1962). Black
polyethylene is used as a high frequency cutoff filter. In general, the
filters are at room temperature. The IR-radiation is mechanically chopped
and guided to the sample through an ½ inch diameter brass pipe. Details

of the sample chamber are shown in Fig. 1. A commercial Rapid Scan Inter-
ferometer (EOCOM, FMS[R] 70001P) has also been used by us to study "deep"
impurities. This instrument is equipped with 2 inch optics, a Nernst
glower as an IR-source, a KBr (Ge) beam splitter and the unit permits 8 cm
mirror travel. Mirror velocity and distance are controlled via a fringe
counting system using a helium-neon laser. A white light interferometer
indicates the zero path position. This instrument covers a frequency range
of 400 to 8000 cm^{-1}. A single PDP-11/20 computer is interfaced to both
the long and the short wavelength interferometers. It performs Fast
Fourier Transformation of up to 4096 points, each with values between $\pm2^{15}$.

Special attention must be given to sample preparation and contacts.
To reduce any chance of contamination by fast diffusing impurities, only
low temperature processes are permissible. Samples cut from single Ge
crystal slices, several mm thick, arc lapped with 1900 mesh alumina, etched
in a 3:1 mixture of HNO_3 (70%) and HF (49%) and rinsed in either methanol
or deionized, distilled water. After this preparation, the samples have
a mirror-like finish. The preparation of Si samples is very similar, ex-
cept that the etch solution has a mixing ratio of 20:1 (HNO_3:HF).

A low-noise contact is produced on high-purity, p-type Ge and n-type
Si by rubbing In-Ga eutectic into opposite faces of the sample. This metal
contact begins to show breakdown at fields of 100 mV/cm which results in
"noisy" spectra. A veteran technique for making pt. contacts involves
indium alloying under a protective argon atmosphere. This has two dis-
advantages: first, the solubility of In in Ge is relatively low, and
second, the energy level of the indium acceptor is deeper than the ones
of B, Al and Ga and it freezes out at higher temperatures. A better con-
tact is based on solid phase epitaxy (SPE). An aluminum layer, evapor-
ated on a very clean Ge surface, can dissolve up to 1% Ge at 350° C
(Caywood et al 1972). During slow cooling (1°/min.), the Ge regrows on
the bulk, incorporating large amounts of Al and producing a thin, highly
doped p^+ layer.

Contacts on n-type Ge are a more difficult problem. The SPE method,
using antimony on n-type Ge, does not work well due to the masking effect
of the thin oxide layer on the Ge surface which prevents the Sb contacting
the Ge in some regions. An interesting discovery was made when an old

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recipe was used to make contacts on n-type Ge. It had been known experi-
mentally that tin alloyed with Ge formed good electron injecting contacts.
The explanation was found in the lithium lines, visible in all spectra
obtained with Ge samples which had tin alloyed contacts. Cross checks
with some samples which had implanted contacts did not indicate the pre-
sence of Li. Tin is obviously a source of lithium.

By far the best low noise contacts are produced by ion implantation.
Boron implanted in Ge (dose: 2×10^{14} cm^{-2}) at room temperature is electri-
cally active "as implanted" (~10%). Heating to 200° C for 1 hour lowers
the contact impedance (Fig. 2). To keep damage to a minimum, we use the
lowest available implantation energy of 25 KeV. Implantation of phospho-
rus in Ge is slightly more difficult. It has been shown (Hubbard et al
1977), that low energy (25 KeV) implantation of phosphorus ions into a
cold Ge sample (77° K), followed by a preannealing stage for several hours
at 150° C and an annealing cycle of 1 hour 350° C, produces a low imped-
ance n-type contact. Fig. 2 shows the dependence of the resistivity of a
pure Ge sample on applied average electrical field for various contacts
on the same sample immersed in liquid helium in the dark.

RESULTS AND DISCUSSION

Elemental Impurities

It would be impossible to detail all the IR spectra obtained from
over 100 different crystals. Suffice it to say that all the dominant
residual impurities in ultra-pure Ge have chemical character. They are
Aluminum, Phosphorus, Boron, and Gallium in descending order of impor-
tance. A typical spectrum can be seen in Fig. 3. The sample size is
0.5 cm^3, the net acceptor concentration is ~ 10^{10} cm^{-3}, and the contacts
are produced by B± ion implantation. The spectrum demonstrates how well
the hydrogenic series of lines of the chemical acceptors can be separated.
The noise level is low enough so that acceptors with concentrations five
hundred times smaller than the main impurity still produce unambiguous
spectra. Aluminum is the dominant acceptor. Traces of boron and gallium
are clearly distinguishable.

Through the systematic study of many crystals grown under a variety
of well-controlled conditions, we have been able to isolate the sources

of the main impurities Al, B and P. We shall only briefly state the results, though a more detailed analysis is found elsewhere (Haller et al 1975). Aluminum is practically non-segregating at the concentration levels observed in high-purity Ge whenever the Ge-melt is contained in quartz. An electrically neutral Al-0 complex has been proposed to exist. In the final crystal, a small fraction of these complexes dissociates, producing free Al which acts as a normal acceptor. In general, we have shown that there is ~ 10 times more Al in quartz crucible grown crystals than is indicated by the Al acceptor concentration. The source of Al can be traced to the intrinsic commercial polycrystalline Ge, which is the starting material used in our process. The sources of boron are all grades of high-purity graphite, pyrolitic carbon coatings and the commercial starting material. Phosphorus is also found in the commercial starting material and in quartz. Synthetic quartz contains the smallest levels of phosphorus, while all natural quartz products dope the Ge melt with $> 10^{12}$ phosphorus atoms/cm^3. The impurities oyxgen, silicon and hydrogen do not produce electrically active centers, but are important in impurity complex formation. Typical concentrations are: oxygen: 10^{13}-10^{14} cm^{-3}; silicon: 10^{15}-10^{17} cm^{-3}; and, hydrogen: 10^{13}-10^{14} cm^{-3}(only in crystals grown in a hydrogen atmosphere. This summarizes the "classical" elemental purity centers.

Non-Elemental, Shallow Hydrogenic Centers

Over the past few years, a number of unknown shallow centers have been found. They can be divided into two groups. The first contains levels which can be associated with one or more crystal growth parameters. The second contains centers which appear in some crystals where no obvious connections with any known crystal parameter can be made.

The first group includes the shallow centers discovered by Hall (1975). He found that the shallow acceptor concentration increases by a few times 10^{11} cm^{-3} when high-purity Ge samples are quenched rapidly (dT/dt > 150°/sec) from temperatures around 400° C. Upon isochronal annealing the acceptor(s) disappear and a donor appear. At approximately 160° C the donor anneals out and the sample returns to its original concentration. We have reproduced Hall's experiment and find that two shallow acceptors, A_1 and A_2, are present after the rapid quench. Figure 5 shows the spectra of the

"as-grown" and the quenched sample. Table 1 contains the line positions of A_1 and A_2. The two hydrogenic series do not correspond to any known elemental impurity acceptor. The donor level which is formed while the acceptors anneal away, is easily observed because it is stable up to ~ 160° C. Only one unknown series of lines (D), which are unusually sharp, can be found in the photoelectric spectrum. This series has already been observed by Secombe and Korn (1972) and Skolnick et al (1974). Using the same sample as Fig. 5, Fig. 6 shows the spectrum after an annealing time of 1 hour at 135° C. The unknown donor is D. Small traces of A_2 are still visible in the spectrum. Recently, we were able to link A_1, A_2 and D to hydrogen in the crystal. A_1, A_2 and D cannot be produced by rapidly quenching crystals which are not grown in a hydrogen atmosphere, nor in thin samples annealed for several hours at 550° C (where hydrogen out-diffusion has occurred). Hall effect measurements over a wide temperature range show that no deep levels are associated with A_1, A_2 and D. This means that we observe single acceptors and a single donor. Experiments are in progress to explore the microscopic structure of A_1, A_2 and D. Contrary to the observations made by Skolnick et al (1974), we have found no correlation between the "quenched-in" donor D and the elemental impurities Al, B and Ga. This applies also to the acceptors A_1 and A_2. It is interesting to note that Hall's "rapid quench" defects are not the only electrically active centers related to hydrogen in Ge. We (Haller et al 1976), have been able to assign the acceptor at E_V+80 meV, which is always present in dislocation free Ge grown in hydrogen to the divacancy-hydrogen complex. In another paper, to be presented at this conference (Haller and Hubbard 1977), we will discuss formation of hydrogen-multivalent acceptor complexes.

A new set of shallow, hydrogenic acceptors (A_3,A_4,A_5) has been discovered in crystals grown in a nitrogen atmosphere, using a pyrolitic carbon coated crucible. Such crystals exhibit low oxygen concentrations. The upper spectrum (Fig. 7) obtained with the "as-grown" sample shows, in addition to the well-known boron and aluminum series, three unknown acceptors (Table 1. A_3,A_4,A_5). A_3 and A_5 have completely disappeared after annealing, but A_4 has only been slightly reduced as can be seen in the lower spectrum (Fig. 7). Hall effect measurements show that the

original net acceptor concentration of 3×10^{11} cm^{-3} drops to about 7×10^{10} cm^{-3} after the sample has been fully annealed at 430° C for 400 hours. In all cases, spectra recorded, using band edge optical pumping, show only the well-known phosphorus series. Only the high-sensitivity and high-resolution of photoelectric spectroscopy allows a clear distinction between A_4 and boron and between A_5 and Gallium! As in the case of the "quenched-in" centers, we have no knowledge of the microscopic structure of A_3, A_4, A_5. It seems that these levels are not related to elemental impurities, such as Al and B.

The second major group of unknown shallow levels cannot be linked to any crystal growth parameters and properties. Fig. 8 shows a spectrum with an unknown hydrogenic series of lines (A_7, Table 1) located between boron and aluminum. The particular crystal #291 contains rather large amounts of copper ($\sim 1.5 \times 10^{11}$ cm^{-3}). It would be tempting to link A_7 to a copper complex, but so far, persuasive clues are lacking. Equally puzzling is an acceptor level A_6 (Fig. 1), which appears at random in many crystals. A_6 was the dominant acceptor only in the use of a sample prepared from a polycrystalline sample from a zone-refined Ge bar. No further explanation for A_6 is available at the present time.

The last ambiguity in the shallow level range concerns lithium in Ge. Li produces two series of hydrogenic donor lines. The lines of the so-called S-series (Hall 1974, Skolnick et al 1974) are very narrow and were assigned to the Li-O-Complex. Extensive work has been done by Bykova et al (1975). Their final assumption is that all Li appears in a complex form. We have performed Electron Paramagnetic Resonance experiments in order to gather additional information. Though this conference is concerned with photoelectric spectroscopy, we believe that the EPR results may stimulate a better understanding of the lithium problem. We found that at low Li-concentrations ($<10^{13}$ cm^{-3}) four absorption lines are produced. Their position depends on the angles between the DC-magnetic field and the crystal axis. This means that donor site is not isotropic. Its symmetry axis lies in the (111) direction. No hyperfine splitting due to the unclear momentum of Li could be detected. Only one set of absorption line s showed up even though photoelectric spectroscopy showed both series of lines by lithium. At higher lithium concentrations, broad features

appeared which are due to Li-clusters. This situation is analogous to the case of antimony in Ge (Hall et al 1975).

Semi-deep elemental acceptors

Accidental contamination by elements forming multivalent acceptors can be efficiently traced by photoelectric spectroscopy, as long as the lowest level is not deeper than $\sim E_V + 50$ meV. Beryllium (Haller and Hansen 1974a) and zinc have been observed in high-purity Ge crystals. Helium-like levels have not been observed with photoelectric spectroscopy. High-resolution helium-like spectra would be of interest to the theory of acceptors in Ge. Advanced calculations by Baldereschi and Lipari (1976) show an ambiguity in the interpretation of the C-line in dydrogenic spectra which could possibly be resolved with high-resolution helium-like spectra. It might also be possible to increase the sensitivity for detection of the second level of double acceptors by counterdoping with a fast diffusing donor to the point where the Fermilevel locks on the level of interest.

A large number of unknown, hydrogenic acceptors have been discovered in the 15 to 30 meV wavelength range. We have been able to synthesize these levels with doping experiments. The results will be reported in another paper to be presented at this conference (Haller and Hubbard 1977).

Hydrogenic, elemental impurities in silicon

Si-results appear modest when compared with the abundance of data obtained with high-purity Ge. In part, this is due to the fact that we are not involved in Si-purification and crystal growth. It does not reflect our interest, not the importance we assign to photoelectric spectroscopy of silicon.

One of the interesting problems in Si-technology is obtaining very homogenous doping. Neutron-irradiation doping is a proven way to achieve this. It is, however, important to begin this process with the purest Si available, since the residual elemental impurity variations will give the lower limit for the homogeneity. We have been able to obtain Si samples* containing $<2 \times 10^{11}$ cm^{-3} boron and $<2 \times 10^{11}$ cm^{-3} phosphorus.

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*We are indebted to Dr. B. Kolbesen, Siemens Ltd., Munich, W. Germany for the high-purity samples and the permission to publish results obtained with them.

At such low concentrations IR-absorption with 1 cm thick slices do not show any lines due to impurities. An additional disadvantage of classical IR-absorption spectroscopy is the need for large size samples with good crystalography. The superior sensitivity of photoelectric spectroscopy can be recognized from the spectra in Fig. 9. With a sample volume of ~ 0.5 cm^3 a signal-to-noise ratio of > 30 was obtained. Boron implanted contacts (150 keV/10^{15} cm^{-2}) annealed at 500° C for 1 hour were used. Spectrum is taken without optical pumping and shows the boron series. Spectra b) and c) were recorded with optical pumping and they show the phosphorus-series. This is a case where minority and majority impurities produce positive going lines. The lifetime of electrons and holes is believed to be long enough for the carriers to traverse the sample.

CONCLUSIONS

Our results demonstrate the vital part photoelectric spectroscopy has played in the development of very pure semiconductors. In addition, a whole, new field has opened, with the possibility of high-resolution detection of very low concentrations of energy levels in the forbidden band of semiconductors. The large number of unexplained acceptors and donors should stimulate considerable experiment and theory of complexes in pure semiconductors. Uniaxial stress experiments and EPR might lead to a better understanding of the microscopic structure of these complexes.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

(1) $\underline{A}$. Interferometer: S=high pressure mercury arc lamp; Mp, Mf and
     Mm are mirrors; Ch=chopper wheel. $\underline{B}$. Cryostat: 1. liquid nitrogen
     cooled glass jacket; 2. liquid helium; 3. cool finger (copper);
     4. heater resistor; 5. brass cavity; 6. Ge-sample; 7. temperature
     sensing carbon composite resistor (56Ω at room temperature; 8. spring
     clip to hold Ge-sample.

(2) Resistance-electric field plot of Ge-sample #S26-7.0. Contact area
     = 2 x 7 mm^2, thickness = 7 mm; LPE = liquid phase epitaxy; SPE =
     solid phase epitaxy N_A-N_D = 10^{11} cm^{-3}.

(3) Photoelectric Spectrum obtained with a typical high-purity Ge sample
     (#313-0.2), contact areas B± implanted = 8 x 8 mm^2, thickness = 8 mm;
     N_A-N_D = 10^{10} cm^{-3}, instrumental resolution = 0.15 cm^{-1}.

(4) Spectrum of the sample used in Fig. (3) but under optical pumping.
     The negative going lines belong to the minority impurity phosphorus (P).

(5) Spectra of an "as grown" and "rapidly quenched" sample (#497-5.5).
     Contact area = 1.2 x 8.0 mm^2, thickness = 8 mm; N_A-N_D (elemental
     impurites) = x 10^{10} cm^{-3}; the hydrogenic series A_1 and A_2 only show
     up in hydrogen-atmosphere grown crystal and do not belong to any
     known acceptors; both spectra show phosphorus lines only under optical
     pumping.

FIGURE CAPTIONS (CONT.)

(6) Spectrum of the sample used in Fig. (5) but after annealing for 1 hour
     at 135° C. The "quenched-in" donor D appears. Its lines are much
     sharper than the ones produced by chemical impurity levels.

(7) Spectra of sample (#495-6.6) of a crystal grown in a nitrogen-atmos-
     phere out of a pyrolitic-granite coated quartz crucible; contact
     area = 4.5 x 7.0 mm^2; thickness = 7.0 mm, N_A-N_D (as grown) = 3×10^{11} cm^{-3},
     N_A-N_D (fully annealed) = 7×10^{10} cm^{-3}, A_3, A_4 and A_5 are hydrogenic
     series of lines produced by unknown levels. They disappear under an-
     nealing.

(8) Spectrum of sample #291-14.0. Hydrogenic series A_7 belongs to an un-
     known acceptor. This crystal contains a relatively high concentration
     of copper.

(9) Spectra of an ultra-pure silicon sample (#88 021-1) contact area =
     9 x 9 mm^2, thickness = 8 mm; N_A, N_D (5×10^{11} cm^{-3}), a) no optical
     pumping b) & c) strong optical pumping. Crystalography was disturbed.

TABLE 1

		Ground state energy in meV	line positions[**] in cm^{-1} ($\pm.01$ cm^{-1})							
		$E^{*}_{g.s.}$ (meV)	D	C	B		A			
"quenched-in", hydrogen related acceptors	A_1	10.24	62.16±.03	68.03±.03	-	-	-	-	-	
	A_2	11.31	70.85	76.89	82.00	83.99	84.71	85.78	86.38	
nitrogen atmosphere, pyrolitic-graphite related acceptors	A_3	9.87	59.22	65.29	-	-	-	-	-	
	A_4	10.42	63.64	69.67	74.79	76.91	77.47	78.50	79.20	
	A_5	10.97	68.03	74.10	79.20	81.40	81.86	-	-	
unknown acceptors	A_6	11.93	75.79	81.85	87.02	89.67	90.89	91.28		
	A_7	10.66	65.57	71.68	76.82	-	-	-	-	

*The ground state energy was determined by adding 2.53 meV to the energy of the D-lines. (Jongbloets et al 1976)

**notation of Jones and Fisher (1965)

***called X by Skolnick et al (1974) but left unexplained.

XBL 7311-1400

FIG. 1

#S26·7.0
T=4.25K

B⁺·IMPL

In·LPE

B⁺·IMPL/ANNEAL

InGa·EUTECTIC

Al·SPE

$\overline{E}$(mVcm^{-1})

$\overline{R}$(MΩ)

XBL 775-8576

FIG. 2

#313-0.2
T=8.0K

XBL 774-8313

FIG. 3

FIG. 4

FIG. 5

XBL 774-8310

FIG. 6

FIG. 7

FIG. 8

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XBL 7310-1396A

FIG. 9

XBL 774-8312