

Zone Leveling and Solution Growth of Complex Compound Semiconductors in Space

Final Report

by

Klaus J. Bachmann

Professor of Chemistry and Materials Science and Engineering
North Carolina State University, Raleigh, NC 27695-8204

Concerning research funded by
NASA Grant NAG 1-354
Langley Research Center
May 1, 1983 - September 30, 1986

1N-76
~~33341~~
35848

Abstract

A research program on complex semiconducting compounds and alloys has been completed that addressed the growth of single crystals of $\text{CdSe}_y\text{Te}_{1-y}$, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$, $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$, $\text{InP}_y\text{As}_{1-y}$ and CuInSe_2 and the measurement of fundamental physico-chemical properties characterizing the above materials. The purpose of this ground based research program was to lay the foundations for further research concerning the growth of complex ternary compound semiconductors in a microgravity environment. This work has resulted in 6 publications, 7 presentations at national and international meetings and supported the completion of a PhD thesis in Materials Science and Engineering by Mr. K. Y. Lay that was successfully defended on 9.26.86. A research proposal concerning a follow-up program incorporating a plan for a future flight experiment is being forwarded to NASA Headquarters at this time.

1. Background Information

During the period from July 1, 1983 to September 30, 1986 we conducted ground based research concerning the growth of bulk single crystals of semiconducting ternary compounds and alloys. The work on alloys relates to infrared optical imaging technology that is of interest to NASA's mission in the

(NASA-CR-179884) ZONE LEVELING AND SOLUTION
 GROWTH OF COMPLEX COMPOUND SEMICONDUCTORS IN
 SPACE Final Report, 1 May 1983 - 30 Sep.
 1586 (North Carolina State Univ.) 28 P.

CSCL 20L G3/76

Unclas
44816

N87-12356

context of satellite based sensors. In particular, $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ is being pursued vigorously as the presently most successful materials system for the fabrication of IR photodiode arrays and a detailed study of bulk crystal growth of this material is presently under way at Marshall Space Flight Center within the framework of NASA's Microgravity Science and Applications program (1,2). Also, a related effort is made at the MIT concerning the growth of CdTe that is the most commonly used substrate for heteroepitaxial growth of $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ (3). Both efforts are meaningful since photoconductive $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ detectors fabricated from bulk single crystals still are important for a variety of IR applications while heteroepitaxial structures are better suited for the fabrication of diode arrays that are the primary sensing elements in focal plane sensor systems. Although the lattice mismatch of HgTe and CdTe, 0.3% at room temperature, is small it still leads to a substantial density of misfit dislocations at the $\text{Cd}_z\text{Hg}_{1-z}\text{Te}/\text{CdTe}$ interface and to concomitant problems in the growth of abrupt double heterostructures and multiple quantum well heterostructures that are desirable for future advances in $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ technology. Therefore, there exists currently considerable interest in exactly lattice matching II-VI alloy substrates that provide for lower defect density and improved metallurgical interfaces. Although we started our program on II-VI alloys with work on $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ bulk crystal growth, we added work on 3 alternative exactly lattice matching II-VI alloys; $\text{CdSe}_y\text{Te}_{1-x}$, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$; that completely cover the lattice constant range in the CdTe-HgTe pseudobinary system for $0 \leq z \leq 1$ and $x, y \leq 0.1$. The phase relations for the above II-VI alloy systems are known and exhibit in the cases of $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{CdSe}_y\text{Te}_{1-y}$ very narrow solidus-liquidus separations for dilute alloys. Therefore, these two systems are suitable for normal freezing type crystal growth techniques. The $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ systems are characterized by wider solidus-liquidus

separations that require the application of zone leveling to achieve axially uniform composition on a macroscopic scale. Therefore, these systems present more complicated cases needing more sophisticated hardware and attention to constitutional supercooling in the selection of the growth rate. In addition, substantial Hg pressure must be sustained in thermal equilibrium with the molten zone for $Cd_zHg_{1-z}Te$ which represents thus the experimentally most complicated case. In view of the above assessment concerning the relative merits of bulk vs. epitaxial $Cd_zHg_{1-z}Te$ and because of the similarity of the fundamental research issues that are to be addressed in the context of materials processing in space in all 4 alloy systems, we tend now to give preference to $Mn_xCd_{1-x}Te$ and $Zn_xCd_{1-x}Te$ for reasons that will be presented more fully in section 2 of this report.

Ternary chalcopyrite structure isoelectronic analogs of the III-V and II-VI compounds of the type II-IV-V₂ and I-III-VI₂ are of general interest for non-linear optics applications since compounds with high figures of merit are known in both classes, e.g. ZnGeP₂ and AgGaS₂, respectively (4). Also, the unusually steep absorption edge of some of the I-III-VI₂ compounds, e.g. CuInSe₂ and CuInS₂, makes these materials interesting candidates for photovoltaic solar energy conversion since the photogeneration of minority carriers proceeds in this case well within the depletion layer leading to almost maximum theoretical collection efficiency even in simple polycrystalline thin film solar cell structures. Although efficient carrier collection alone is not sufficient to guaranty high power conversion efficiency, thin film CuInSe₂/Zn_xCd_{1-x}S solar cells with 12.5% power conversion efficiency a AM1 and excellent stability have been reported by several industrial research groups (5). Also, CuInSe₂ based solar cells are unusually resistant to radiation damage. Because of this property and the light weight of thin film CdS/CuInSe₂ or ZnO/CuInSe₂ cells they are of potential use for space applications. Further improvements by the

utilization of I-III-VI₂ alloys and tandem cell structures in combination with -Si:H appear to be possible which motivated an extensive study of the fundamental properties of CuInSe₂ (7-10) and its alloys with CuInS₂ (11,12) and CuGaSe₂ (13) in our laboratory. A major part of this work was pursued under contract with SERI, and we comment in this report only on those aspects of our research that are relevant to the microgravity related research covered in this project. There exists a considerable incentive for continuing research on CuInSe₂ in the context of materials processing in space since this material represents a model case for the melt growth of a non-cubic semiconductor with specific problems that could be overcome in a microgravity environment and that will have a significant impact on other technological developments. Further details will be presented in sections 3 and 4.

In addition to the above work on II-VI alloys and on their I-III-VI₂ isoelectronic analogs we pursued research concerning InP_yAs_{1-y} and CdSnP₂ that are examples of III-V ternary alloys and their II-IV-V₂ isoelectronic analogs. Although we continue to have an interest in these two systems we believe that in view of the high decomposition pressures and safety risks in handling InP_yAs_{1-y} and the limited access to experimentation in space the above identified II-VI and I-III-VI₂ systems are more important for further exploration. For an assessment of critical research issues concerning the above ternary compounds and alloys we refer to the attached preprint of an invited paper presented at the 7th International Conference on Ternary and Multinary Compounds, Snowmass, Colorado, September 10-12, 1986 (14).

2. Training of Graduate Students, Research Interactions and Conference Presentations

The funding provided by this grant supported fully the research of one graduate student of Materials Science and Engineering, Mr. K. Y. Lay and helped through research interactions in the education of three other graduate stu-

dents, Ms. N. Giles-Taylor and Mr. K. Park in the Department of Physics, and Mr. B. Abid in the Department of Chemistry. Mr. Lay started his thesis on The Growth and Characterization of CdTe-Based II-VI Alloys in May 1983 and successfully defended this thesis on September 26, 1986. He has accepted a position at II-VI Inc., Saxonburg, Pennsylvania where he will pursue further research on II-VI alloy systems for infrared applications.

Three post-docs, Dr. P. Lange and Dr. H. Goslowsky from the Hahn-Meitner Institut, Berlin, FRG and Dr. H. Neff of Brown Boveri & Cie, Baden, Switzerland, who were supported primarily through other research programs contributed to the research covered by this report. Also, we acknowledge the expert help of Prof. J. F. Schetzina and Prof. G. Lucovsky of the Department of Physics at NCSU in our early photoluminescence studies and in the XPS measurements, respectively. The UPS measurements on our $Mn_xCd_{1-x}Te$ were performed by Dr. R. Kotz of Brown Boveri & Cie, at Baden, Switzerland.

The results of our work were presented by Mr. Lay at the First State-of-the-Art Program on Compound Semiconductors (SOTAPOCS), ECS Meeting, New Orleans, Louisiana, October 9-10, 1984 and at the MRS Workshop on Materials Characterization, Research Triangle Park, NC, September 17, 1985. The PI presented a contributed paper at the International Conf. on Crystal Growth, York, England, July 14-16, 1986 and two invited papers at the PVA R&D Meeting, Denver, Colorado, May 13-15, 1986 and at the 7th International Meeting on Ternary and Multinary Compounds, Snowmass, Colorado, September 10-12, 1986. Further presentations by Mr. Park at the MRS Symposium on Diluted Magnetic (Semimagnetic) Semiconductors and an invited paper by the PI at the MRS Symposium on Materials for Infrared Detectors and Sources will be included into the Fall Meeting of the MRS, December 1-6, 1986 at Boston, Massachusetts.

3. Technical Results

The growth of $\text{CdSe}_y\text{Te}_{1-y}$, $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ and CuInSe_2 crystals was carried out in a modified vertical Bridgman furnace while $\text{InP}_y\text{As}_{1-y}$ and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ were grown by horizontal zone leveling, in the latter case using liquid encapsulation with B_2O_3 to counteract physical vapor transport from the molten zone to the colder parts of the fused silica enclosure. Photoluminescence and electron microprobe scans of the II-VI alloys showed axially uniform composition of the alloys on a macroscopic scale although striations on a microscopic scale were revealed by etching for $\text{InP}_y\text{As}_{1-y}$. The PL spectra of the three II-VI alloys show deep luminescence features corresponding to the 1.42 eV deep emission in CdTe that is shifted by the band gap change of the alloys. This result is consistent with the interpretation of this deep luminescence as D-A transitions with minimum shifts in the depth of the relevant donor and acceptor levels upon alloying. However, in several alloy crystals, particularly $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ for $x < 0.2$, no deep emission was observed. Also, room temperature band to band emission was observed in selected crystals of $\text{CdSe}_y\text{Te}_{1-y}$, $0 \leq y \leq 0.10$. The twinning probability for comparable alloy concentration increased in the order $\text{CdSe}_y\text{Te}_{1-y}$, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$, $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ while the microhardness increased in the order $\text{CdSe}_y\text{Te}_{1-y}$, $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$. For further details we refer to the attached reprint of ref. 15. A study of the broadening of both the PL and photoreflectance (PR) signals shows that up to 20% Mn the spectra are dominated by alloy broadening while at higher concentrations extended defects become dominant (see attached reprint of ref. 16). Recent unpublished transmission electron microscopy studies reveal that these defects are planar domains of ~ 40 A thickness and up to 5000 A diameter that we characterize tentatively as microtwins. Figure 1 shows such microtwins in $\text{Mn}_{0.3}\text{Cd}_{0.7}\text{Te}$. However, although the published phase diagram of the pseudobinary system CdTe-MnTe (17) suggests stable zincblende structure solid solutions up to $x = 0.75$ recent total energy

calculations (18) show that $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ should separate into CdTe and MnTe. Since the computation refers to zero K it does not necessarily pertain to room temperature, but further studies of the phase relations of the $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ system below the solidus is needed to clarify this matter. Because of the controversy concerning alloys with $x > 0.5$ we restricted our investigation to $x \leq 0.45$. However, even for the dilute alloys that are suitable for substrate applications in conjunction with $\text{Cd}_2\text{Hg}_{1-z}\text{Te}$ solving the problem of twinning would be a major breakthrough in the technology.

Since the substitution of Cd^{2+} by paramagnetic Mn^{2+} introduces localized magnetic moments there exist in $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ solid solutions interesting spin-spin interactions between these localized magnetic ions and the extended states. Figure 2 shows results of PL and photoconductivity (PC) measurements that reveal for the first time decayed exciton contributions to the PC of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. The binding energy of the exciton decreases with increasing temperature in accord with the PL results in ref. 19 that suggest a magnetic localization of the excitons by interactions between the hole spin with the Mn^{2+} . The shift of the binding energy towards the position of the free exciton line is thus explained as an increasing excitation of magnetically localized excitons into the free exciton state.

Figure 3 shows the PC spectra for the same crystal at higher T. Note that after a maximum at 100K the PC gain decreases to ~160K and increases at higher T, i.e. it has a minimum at ~2.0 eV. Figure 4 shows PL spectra of $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ as a function of x revealing 2.0 eV emission even at energy gaps $E_g < 2$ eV. This emission becomes dominant at values of x where $E_g > 2$ eV. The above observations establish unequivocally the existence of p-d transitions, i.e., the communication of the Te p-level derived valence band edge with normally empty Mn d electron states that under the conditions of an optical transition

are located 2.0 eV above the valence band edge. The increasing band gap with increasing x is due to the upwards shift of the s -like conduction band edge upon replacement of $Cd(5s)$ by $Mn(4s)$ in the zincblende structure as indicated in the insert in fig. 5. The minimum of the PC near $E_g = 2.0$ eV is interpreted in terms of s - d exchange that has a maximum when the CBE coincides with the energetic position of the $Mn d$ states. Also, the normal behavior in the PL at $E_g < 2.0$ eV reflects the usual excitation behavior between the VBE and the CBE while at $E_g > 2.0$ eV where the s -like CBE is located in energy above the $Mn d$ states the latter act as a trap for photoexcited carriers dominating the recombination behavior. Since hot electrons trapped in $Mn d$ states can recombine even before they are located in energy below the CBE, above band gap 2.0 eV emission is observed for dilute alloy compositions. It should be mentioned that the above information is in conflict with the prevailing interpretation of optical transitions in $Mn_xCd_{1-x}Te$ that are explained as intraion d - d^* transitions (20). However, our results are consistent with recent unpublished band structure calculations by Wei and Zunger that predict p - d transitions near 2.0 eV and d - d^* transitions at higher energies (21). Although clearly being a side product the above work is thus contributing to the understanding of the fundamental physical properties of diluted magnetic semiconductors which in view of their unusual magneto-optical properties deserve further attention.

In the context of substrate applications in $Cd_zHg_{1-z}Te$ heteroepitaxy fundamental physical studies are important for the selection of the optimum material out of the 3 alloy systems under consideration. Because of the favorable microhardness of $Zn_xCd_{1-x}Te$ current crystal growth efforts by others almost exclusively focuses on this alloy. However, mechanical durability is not the only or even the most important selection criterion. For example, for successful epitaxy the native oxide and a layer of defective material under the native oxide generally must be removed by means commensurable with the epitaxial

method, i.e. in view of the strong emphasis of MBE for $\text{Cd}_2\text{Hg}_{1-z}\text{Te}$ epitaxy under UHV conditions. An XPS study of the 3 alloys reveals that the native oxide on $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{CdSe}_y\text{Te}_{1-y}$ is primarily TeO_2 as in the case of pure CdTe, but the native oxide on $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ consists of a mixture of MnO_x and TeO_2 (see the attached reprint of ref. 22). In the case of $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ a double beam PC technique reveals the existence of a 400 meV deep trap below the CBE and a considerable enhancement of the surface recombination rate for the oxidized surface (compare the attached preprint of ref. 23 for details). Although similar studies for $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{CdSe}_y\text{Te}_{1-y}$ are still incomplete detrimental surface properties are, also, expected after oxidation for these alloys.

As favorable method for the fabrication of oxide free clean surfaces we explored sputter cleaning combined with subsequent low temperature annealing of the substrates. As shown in ref. 22 (see attached reprint) $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ is far less susceptible to damage than pure CdTe and recovers after 30 min annealing at 200°C to the undamaged state while the CdTe lattice cannot be restored at 200°C even on extended annealing cycles. PL spectra reveal the generation of shallow and deep defect levels in CdTe, but only a slight increase in the concentration of shallow levels in $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ after sputter cleaning. Both $\text{CdSe}_y\text{Te}_{1-y}$ and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ damage substantially during sputter cleaning as demonstrated by figs. 6-12 that show the PL spectra and PR spectra prior and after 5 kV Ar^+ exposure to comparable dose for the 3 alloys under consideration (24). Although the annealing studies on $\text{CdSe}_y\text{Te}_{1-y}$ and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ are still outstanding the information gathered thus far favor $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ over $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ in terms of their surface properties. An issue that has not been addressed yet and is of considerable importance for the development of devices is the relative response of the two materials systems to extrinsic doping. Since $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ are nominally undoped of p-type and n-type conduc-

tivity, respectively, and compensation is expected to be associated with difficulties the preferred substrate choice may depend on the application. However, more work is required to clarify this point.

In order to perform intelligent crystal growth on ternary compound semiconductors detailed knowledge of their phase diagrams is imperative. Figure 13 shows the liquidus surface of the Cu,In,Se system (7) that exhibits extended regions of immiscibility in liquid state which must be avoided during the synthesis stage of the compound from $\text{Cu}_{.5}\text{In}_{.5}$ and elemental selenium. Appropriate procedures for doing this are established in our laboratory. Also, fig. 13 reveals that all congruently melting ternary compounds in the system are located at the $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ pseudobinary. Figure 14 shows the $T-x_{\text{In}_2\text{Se}_3}$ diagram on this pseudobinary cut in the range $0 \leq x \leq 0.5$. Note that the maximum melting point on this pseudobinary is on the In_2Se_3 -rich side of CuInSe_2 that consequently cannot be grown from the stoichiometric melt. Control of the stoichiometry is obtained by zone leveling using a Cu-rich liquidus composition and is extremely important in this materials system because of the wide γ phase region that extends several % to In_2Se_3 rich composition at room temperature. The properties of CuInSe_2 depend drastically on the position within the homogeneity range which is documented in detail in refs. 8-10.

In the context of the Microgravity Science and Applications program the following problems of CuInSe_2 crystal growth are of interest: 1. In horizontal zone leveling experiments under ground based conditions it is difficult to suppress nucleation on the boat walls (preferably pyrolytic BN). Since the growth rate of CuInSe_2 is highly anisotropic (slowest perpendicular to the (112) face) the texture of the polycrystalline skin generated on the walls favors their overgrowth by a single crystalline sheet nucleated with (112) parallel to the free surface. The thickness of this sheet is maximized by a vertical gradient keeping the top surface at a lower temperature than the bottom of the

boat. However, such a gradient presents unfavorable conditions with regard to convective cell formation, and completely single crystalline ingots cannot be made at this time. This in turn causes problems related to saving the crystal through the solid state transformations at 850°C and 810°C, respectively, that are revealed by DTA (compare fig. 10) and to prevent crack formation during cooling to room temperature. 2. Vertical Bridgman growth is more successful than horizontal zone leveling to obtain single crystals, but does not provide for axially uniform composition. Even in Bridgman growth the generation of a convex solid-liquid interface is difficult and distortions either in the form of a thin polycrystalline peripheral region or twinning are observed due to container effects on the interface shape. We believe that these difficulties can be circumvented under microgravity conditions where decoupling of the molten zone is possible as described in our original proposal. In view of the value of a supply of stoichiometric well characterized crystals for research and development efforts on CuInSe₂ based devices, particularly in the context of further assessments of the utility of this material in a hostile radiative environment, there exists considerable interest in improved growth methods that may become available as part of NASA's Microgravity Science and Applications program.

4. Proposed Future Work

Based on the above data we believe that a more focussed follow-up program would be meaningful on the growth of Mn_xCd_{1-x}Te by the Bridgman method and of CuInSe₂ by zone leveling. In our opinion, space approved hardware that essentially exists at present or is under active development at Marshall Space Flight Center would be suitable for an experiment with Mn_xCd_{1-x}Te. A substantial arsenal of characterization tools and experience with this material exists at the PI's laboratory so that the apparatus and procedures for comprehensive

characterization of crystals grown in a microgravity environment are in place. Before such an experiment is executed modeling should be performed of the chosen geometry. Although certain experiments on the ground in support of modeling and computer simulations of the planned space experiment will be necessary in the initial phase of a follow-up program planning for such an experiment could resume immediately.

A continuing effort on zone leveling appears to be desirable, but should focus on CuInSe_2 which is of larger significance as compared to $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ in terms of potential for generating new scientific information. In both $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ and CuInSe_2 crystal growth the decoupling of the melt from the container walls will be the key issue for requesting access to a microgravity environment. As has been shown for both $\text{Cd}_z\text{Hg}_{1-z}\text{Te}$ (25) and CdTe (2) container effects are important in the control of the interface shape and may affect the convective flow in both Bridgman and zone leveling geometries. Also, container interactions greatly affect the quality of both CuInSe_2 and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystals grown at 1 g by assisting the nucleation of twins and polycrystalline peripheral regions. The effects of at least partial decoupling of the melt from the container can be studied at 1 g and work on this aspect is incorporated into the research plan for ground based activities in the first 12-18 months of the schedule of work of the proposed continuation. Also, in this schedule we include exploratory research on compensation doped InSb that has not been part of the present activity. In terms of capital equipment expenditures this added activity will not require extra funds since the growth and characterization tools are already established in the context of the above program on $\text{Mn}_x\text{Cd}_{1-x}\text{Te}$ and CuInSe_2 .

References

1. S. L. Lehoczky and F. R. Szofran, *Materials Processing in the Reduced Gravity Environment of Space*, Vol. 9, G. E. Rindone, ed., North Holland Publ., NY 1982, p. 409.
2. R. K. Crouch, *Microgravity Science and Applications, Report on a Workshop*, Pasadena, CA, 1984, National Academy Press, Washington, DC, 1986.
3. T. Jasinski and A. F. Witt, *J. Crystal Growth* 71, 295 (1985).
4. J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Structure Semiconductors: Growth, Electronic Properties and Applications*, Pergamon Press, Oxford, 1975.
5. R. A. Mickelsen and W. S. Chen, *Proc. 16th IEEE Photovolt. Specialists Conf.*, San Diego, CA, 1982, p. 481.
6. D. L. Morell, K. Mitchell, R. Wieting, R. Potter, C. Eberspacher, D. Tanner and C. Fairchild, *Conf. Rec. 18th IEEE Photovolt. Specialists Conf.*, Las Vegas, NV, 1985, p. 876.
7. K. J. Bachmann, M. L. Fearheiley, N. Tran and Y. H. Shing, *Appl. Phys. Lett.* 44, 407 (1984).
8. P. Lange, H. Neff, M. Fearheiley and K. J. Bachmann, *J. Electrochem. Soc.* 132, 2281 (1985).
9. P. Lange, H. Neff, M. Fearheiley and K. J. Bachmann, *Phys. Rev. B* 31, 4074 (1985).
10. M. L. Fearheiley, Y. H. Shing, S. Vasquez, C. Herrington and K. J. Bachmann, *J. Electron. Mater.* 14, 677 (1985).
11. H. Neff, P. Lange, M. L. Fearheiley and K. J. Bachmann, *Appl. Phys. Lett.* 47, 1089 (1985).
12. P. Lange, H. Neff, M. L. Fearheiley and K. J. Bachmann, *J. Electron. Mater.* 14, 667 (1985).
13. B. Abid, H. Neff and K. J. Bachmann, *J. Electrochem. Soc.* 1986, submitted.
14. K. J. Bachmann and H. Goslowsky, *Proc. 7th Int. Conf. on Ternary and Multinary Compounds*, S. Deb and A. Zunger, eds., Snowmass, CO, 1986, to be published.
15. K. Y. Lay, N. Giles-Taylor, J. F. Schetzina and K. J. Bachmann, *J. Electrochem. Soc.* 133, 1049 (1986).
16. K. Y. Lay, H. Neff and K. J. Bachmann, *phys. stat. sol. (a)* 92, 567 (1985).
17. R. Triboulet and G. Didier, *J. Crystal Growth* 52, 614 (1981).
18. S. H. Wei and A. Zunger, *Phys. Rev. Lett.* 56, 2391 (1986).

19. H. Neff, K. Y. Lay, R. Kotz and K. J. Bachmann, J. Lumin. 1986, accepted.
20. Y. R. Lee and A. K. Ramdas, Solid State Commun. 51, 861 (1984), R. Y. Tao, M. M. Moriwaki, W. M. Becker and R. R. Galazka, J. Appl. Phys. 53, 3772 (1982).
21. S. H. Wei and A. Zunger, private communication of unpublished results.
22. H. Neff, K. Y. Lay, B. Abid, P. Lange, G. Lucovsky, and K. J. Bachmann, J. Appl. Phys. 60, 151 (1986).
23. K. Park, H. Neff and K. J. Bachmann, Proc. MRS Symp. Diluted Magnetic (Semimagnetic) Semiconductors, Aggarwal, ed., 1986, to be published.
24. K. Y. Lay, H. Neff and K. J. Bachmann, unpublished results.
25. R. J. Naumann and S. L. Lehoczky, J. Crystal Growth 61, 707 (1983).

ORIGINAL PAGE IS
OF POOR QUALITY



Figure 1. A TEM photograph of a crystal of $\text{Cd}_{0.7}\text{Mn}_{0.3}\text{Te}$.

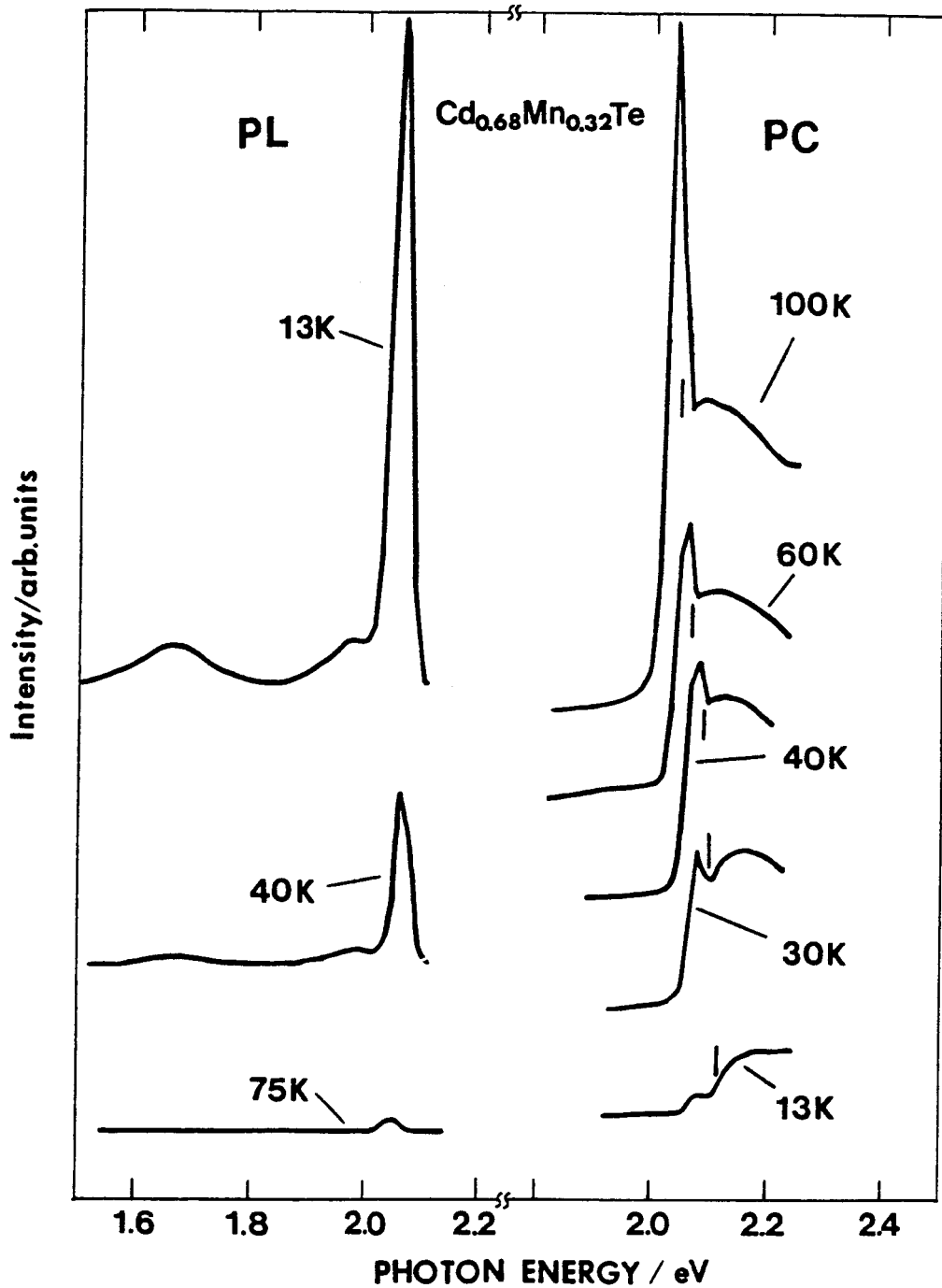


Figure 2. Photoluminescence (left side) and photoconductivity spectra (right side) recorded in the temperature regime $13\text{K} \leq T \leq 100\text{K}$. The band gap position is denoted by a vertical bar in the PC spectra.

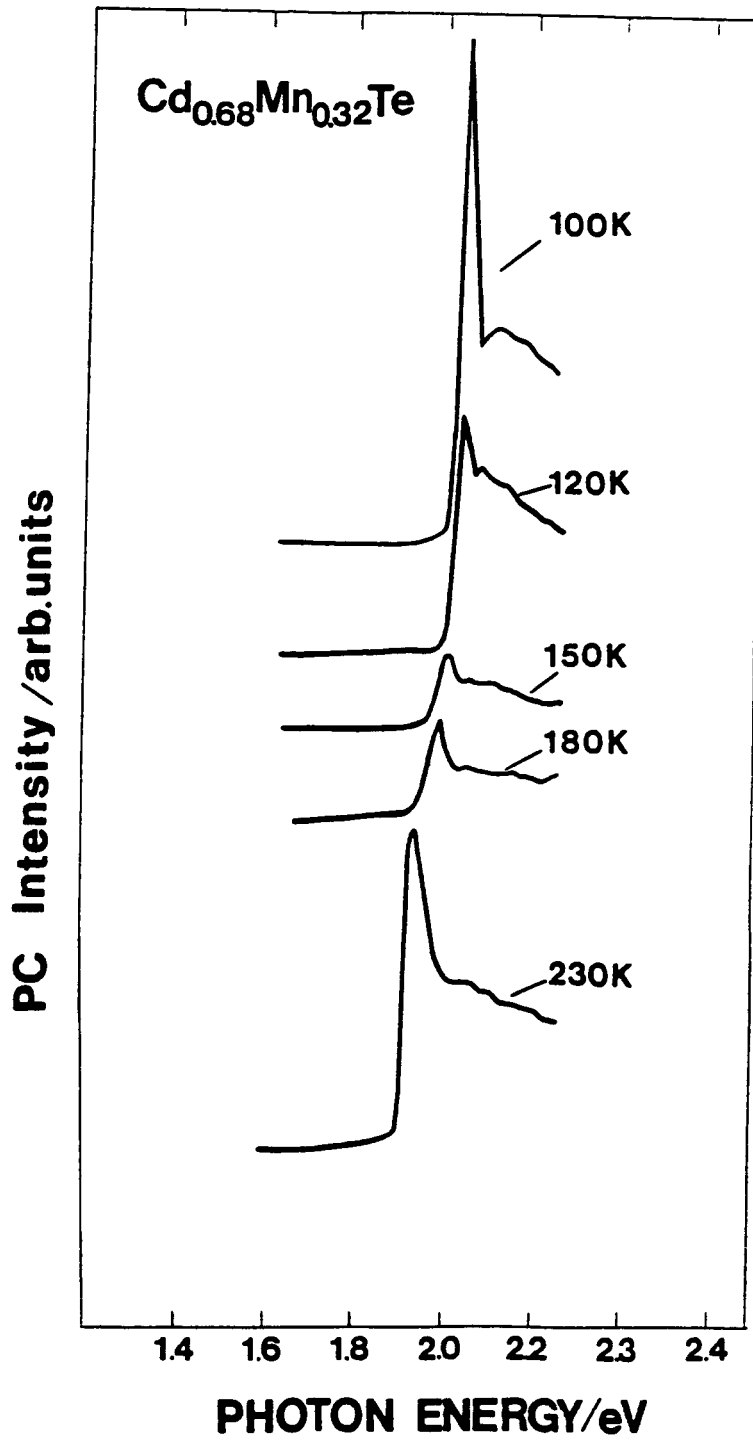


Figure 3. Photoconductivity spectra recorded in the temperature regime $100\text{K} \leq T \leq 230\text{K}$.

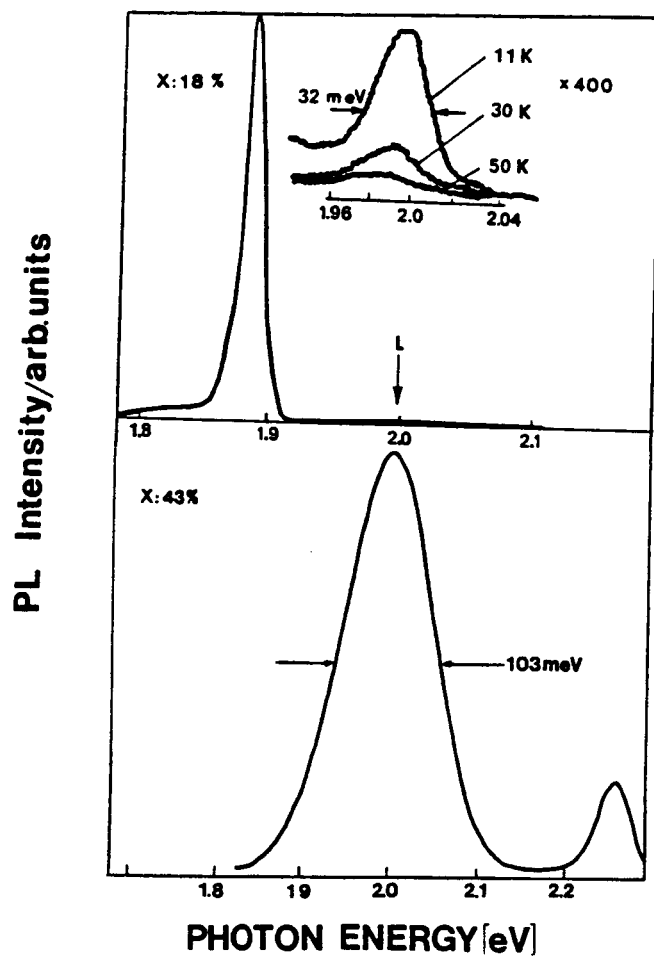


Figure 4. Photoluminescence spectrum obtained at 12K for $\text{Cd}_{0.82}\text{Mn}_{0.18}\text{Te}$. Note the expanded PL-signal centered at 1.99 eV that occurs 100 meV above the excitonic PL-band at 1.9 eV.

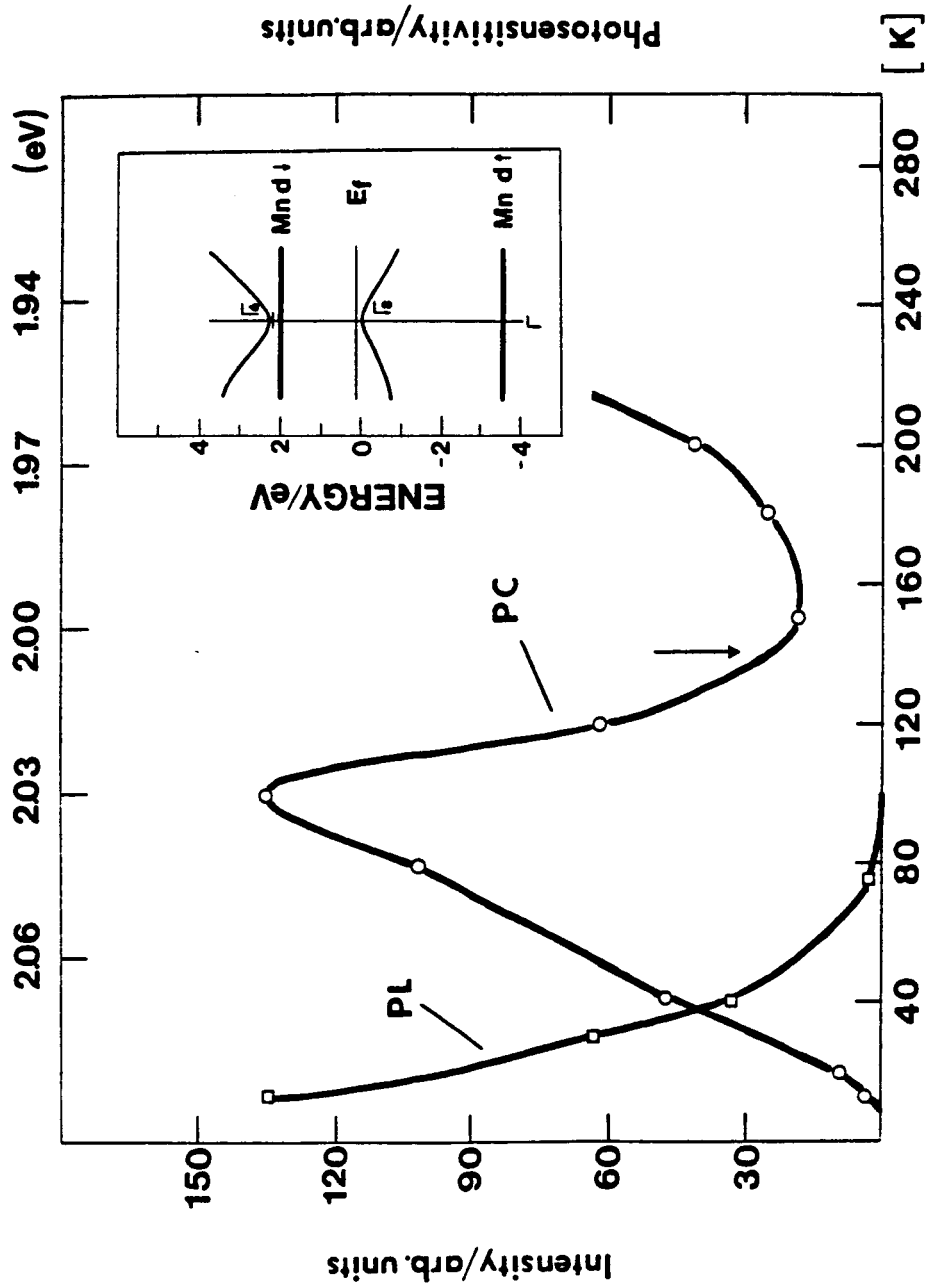


Figure 5. Temperature dependence of the excitonic PC and PL signal. The upper scale shows the position of the (temperature dependent) band gap. The insert shows the $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ band structure around the Γ -point and displays the positions of the spin-split Mn 3d-levels.

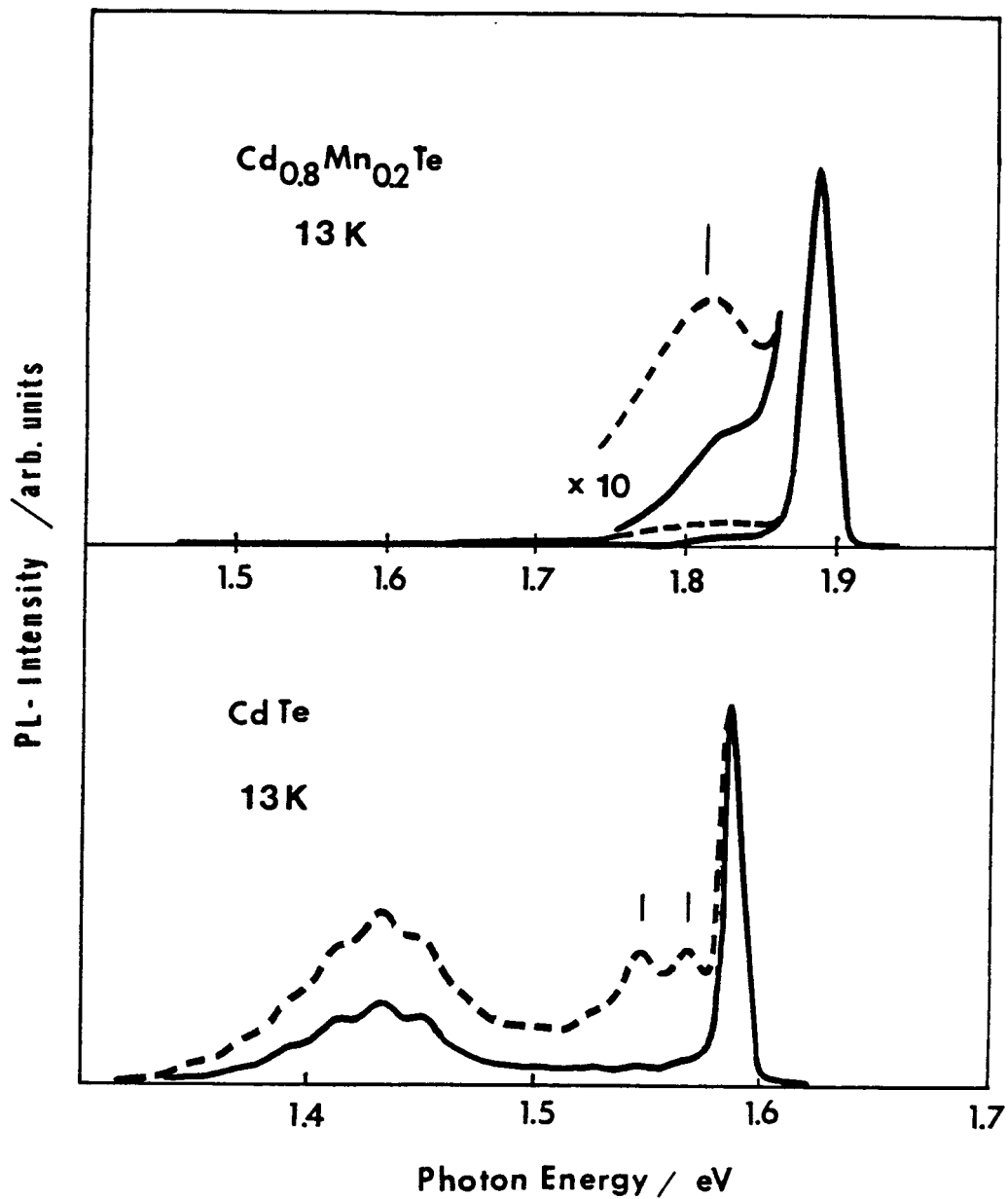


Figure 6. The photoluminescence spectra of CdTe and $\text{Cd}_{0.8}\text{Mn}_{0.2}\text{Te}$ in the as cleaved (full lines) and (110) oriented surface and the surface upon 30 min Ar-ion sputtering (dashed lines).

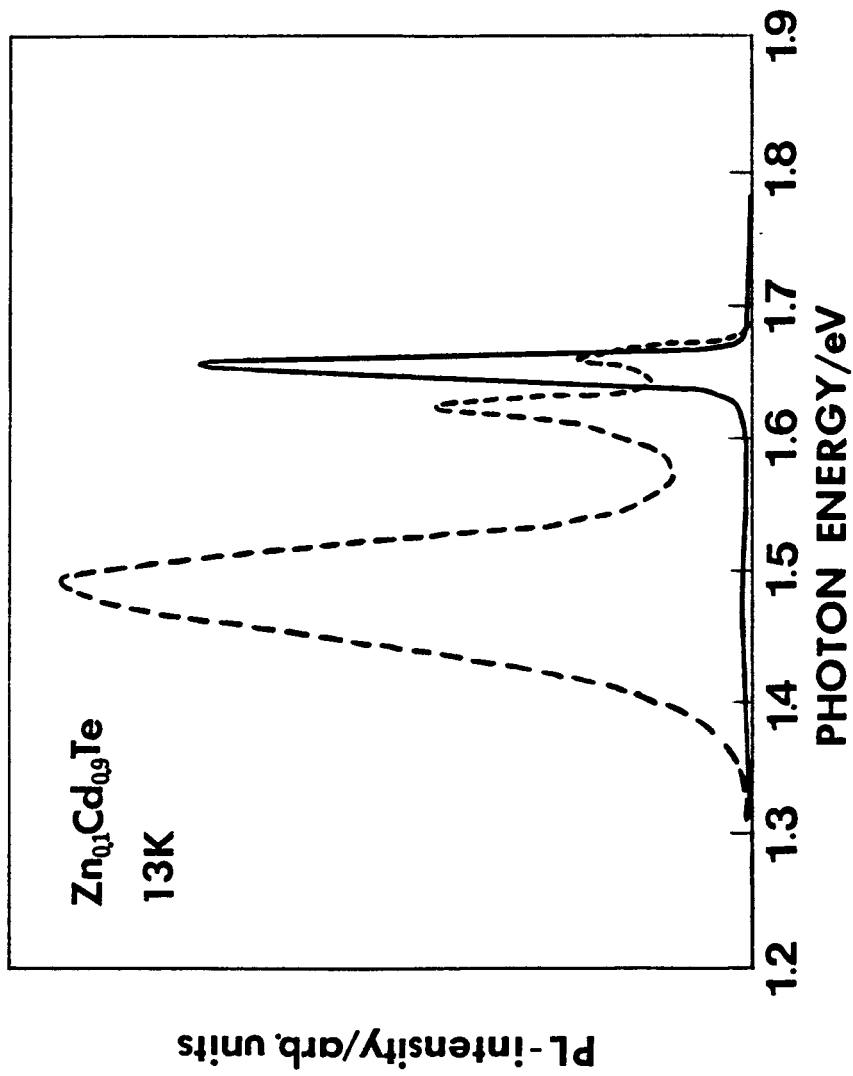


Figure 7. The PL spectra of $Zn_{0.1}Cd_{0.9}Te$ in the as cleaved (full line) and sputtered state (dashed curve) at 13K.

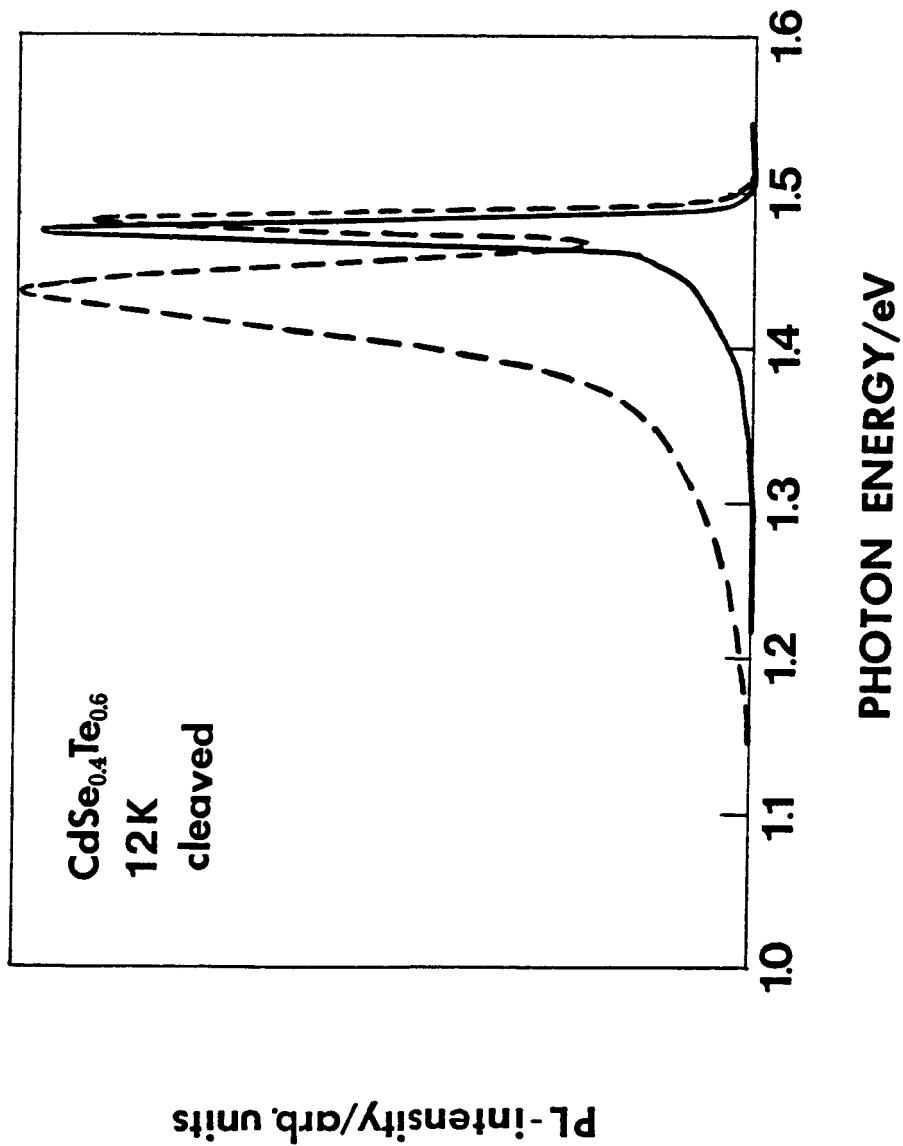


Figure 8. The PL spectra of $\text{CdSe}_{0.4}\text{Te}_{0.6}$ in the as cleaved (full line) and sputtered state (dashed curve) at 13K.

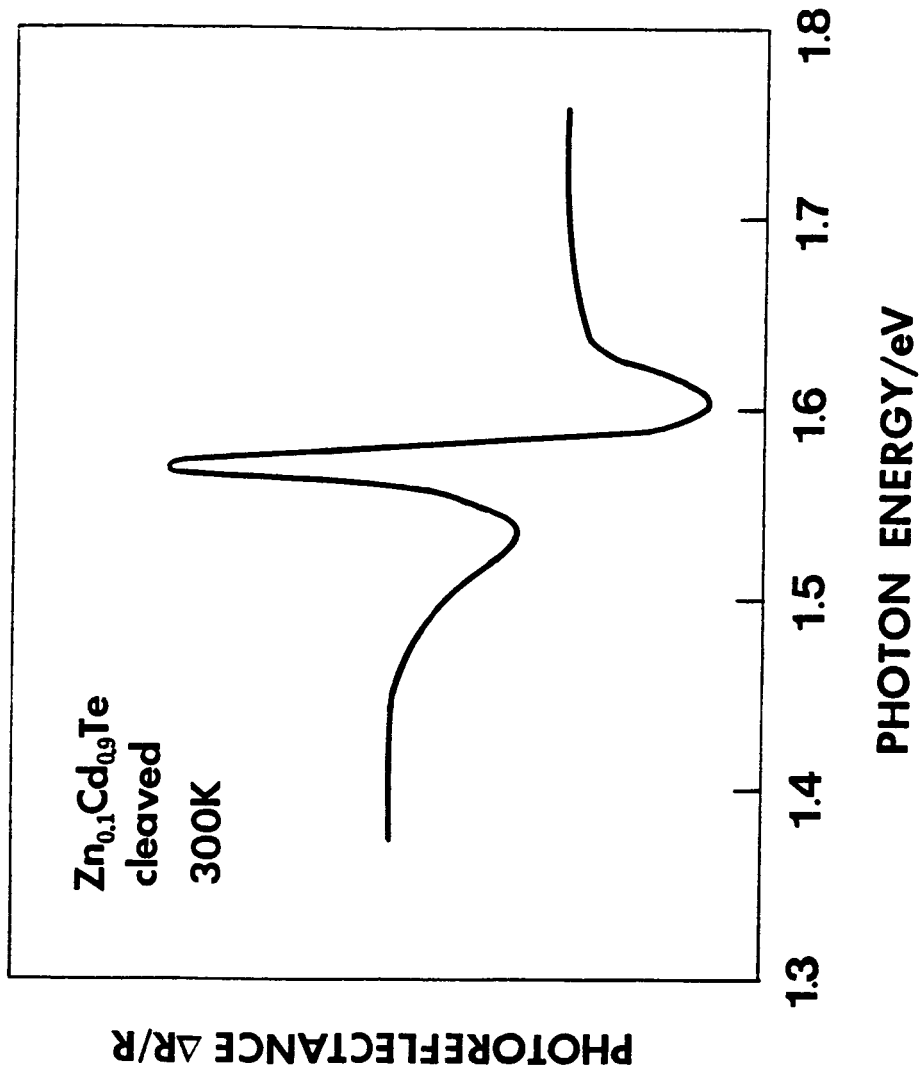


Figure 9. The PR spectra of Zn_{0.1}Cd_{0.9}Te in the as cleaved sample.

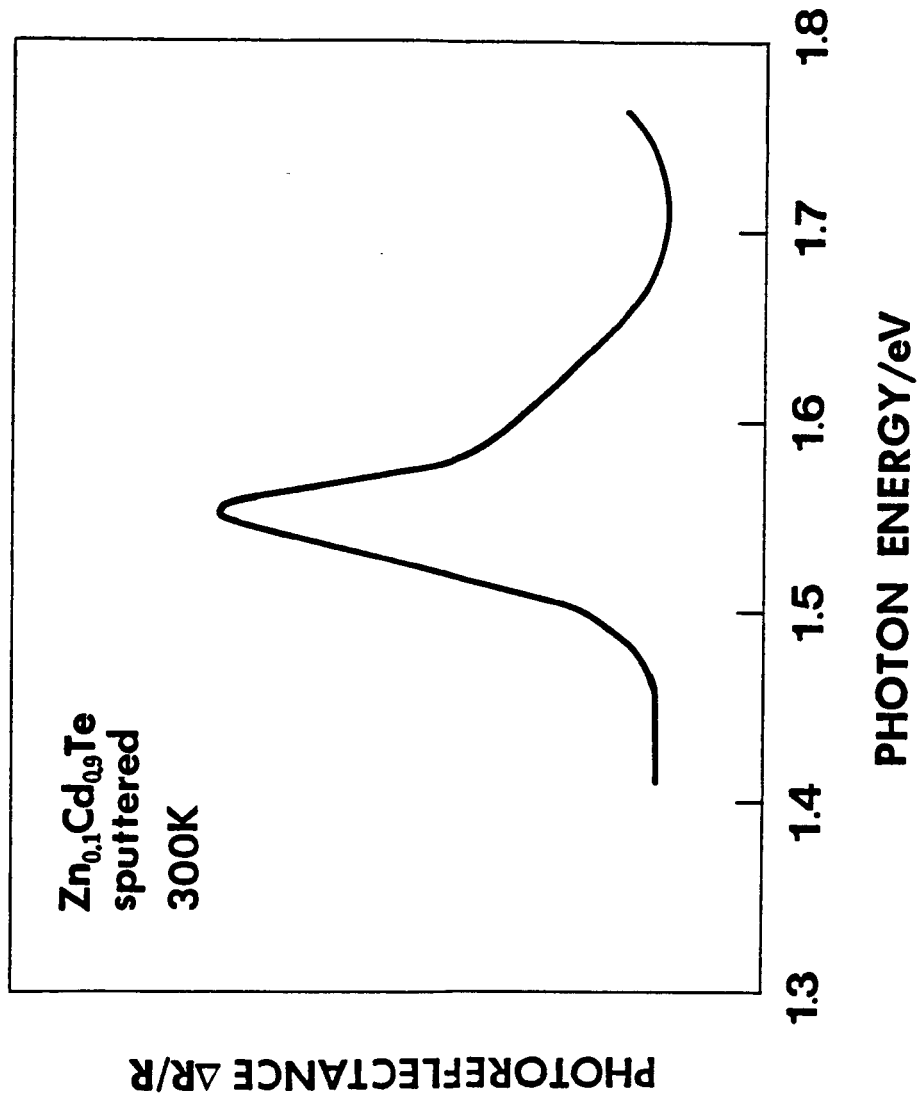


Figure 10. The PR spectra of Zn_{0.1}Cd_{0.9}Te in the sputtered sample.

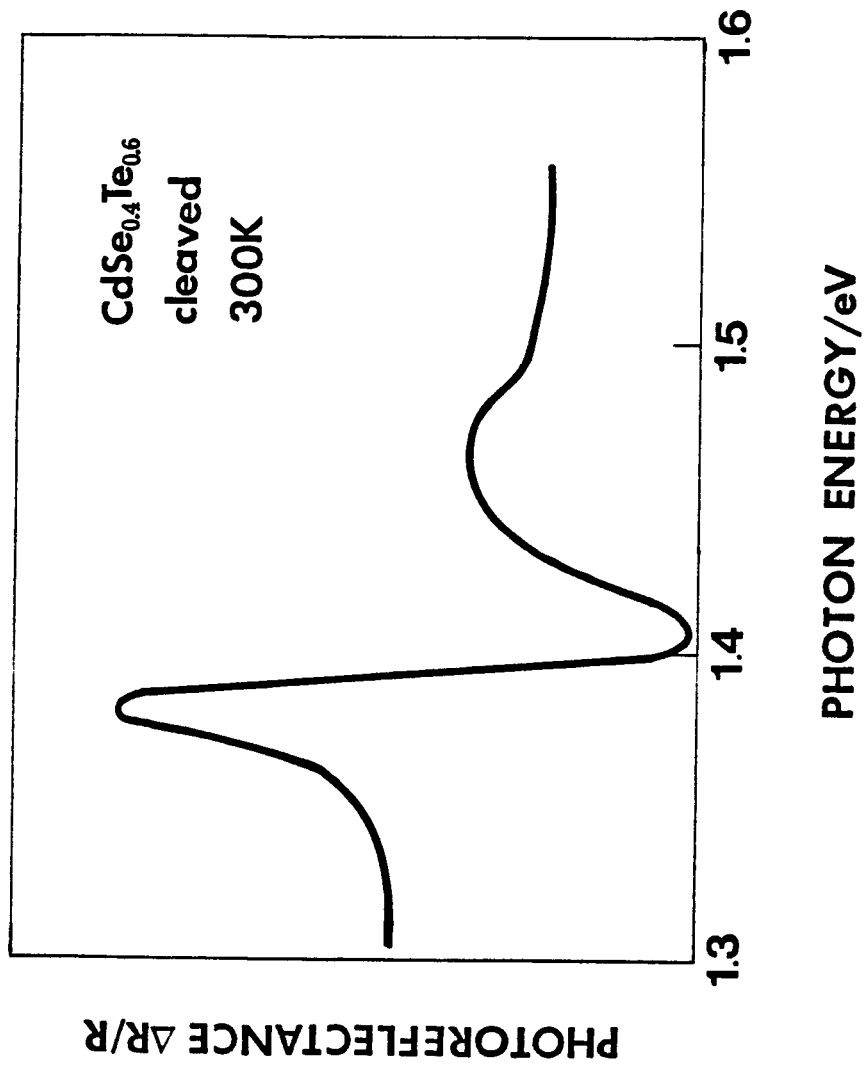


Figure 11. The PR spectra of CdSe_{0.4}Te_{0.6} in the as cleaved sample.

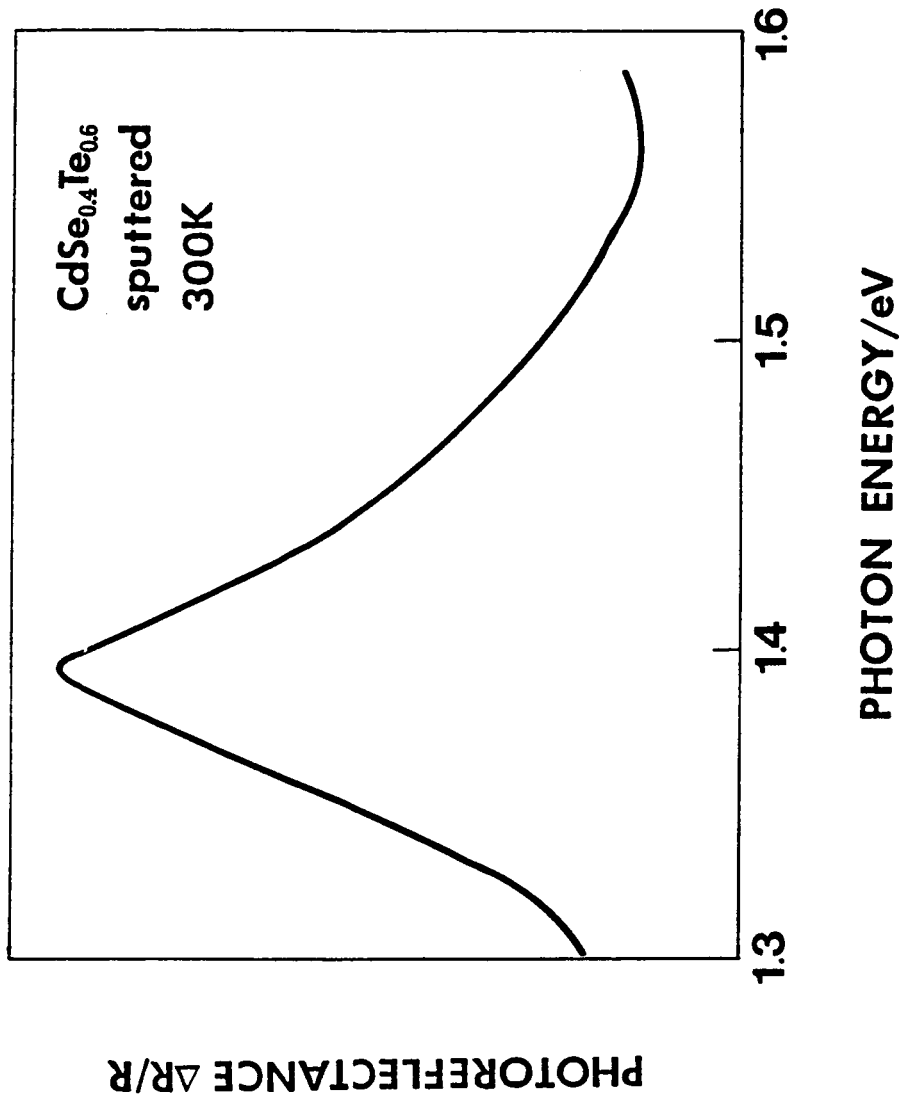
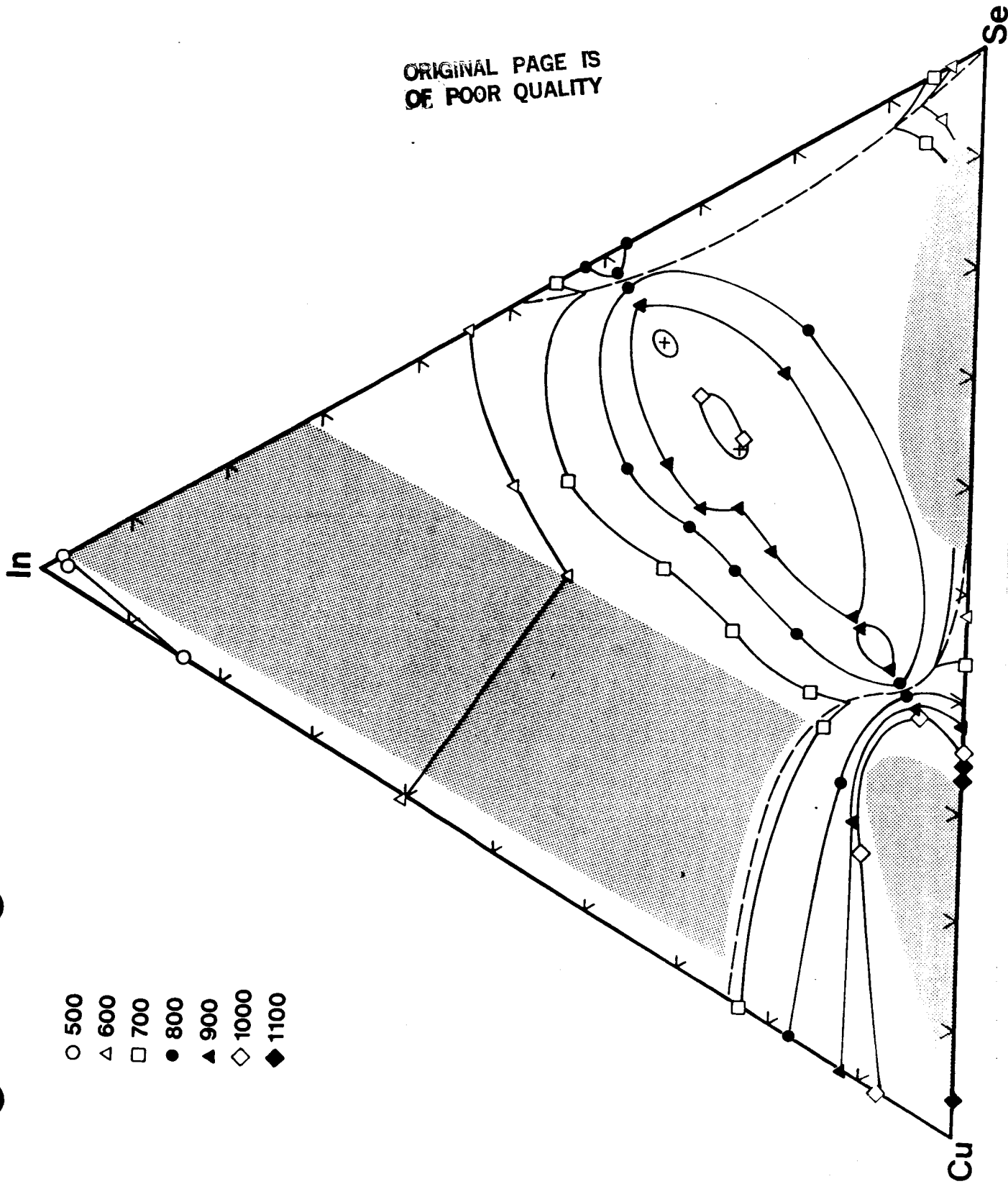


Figure 12. The PR spectra of CdSe_{0.4}Te_{0.6} in the sputtered sample.

ORIGINAL PAGE IS
OF POOR QUALITY



- 500
- △ 600
- 700
- 800
- ▲ 900
- ◇ 1000
- ◆ 1100

Fig. 13 Liquidus Isotherms on Regions of Immiscibility in Liquid State in the Cu, In, Se System

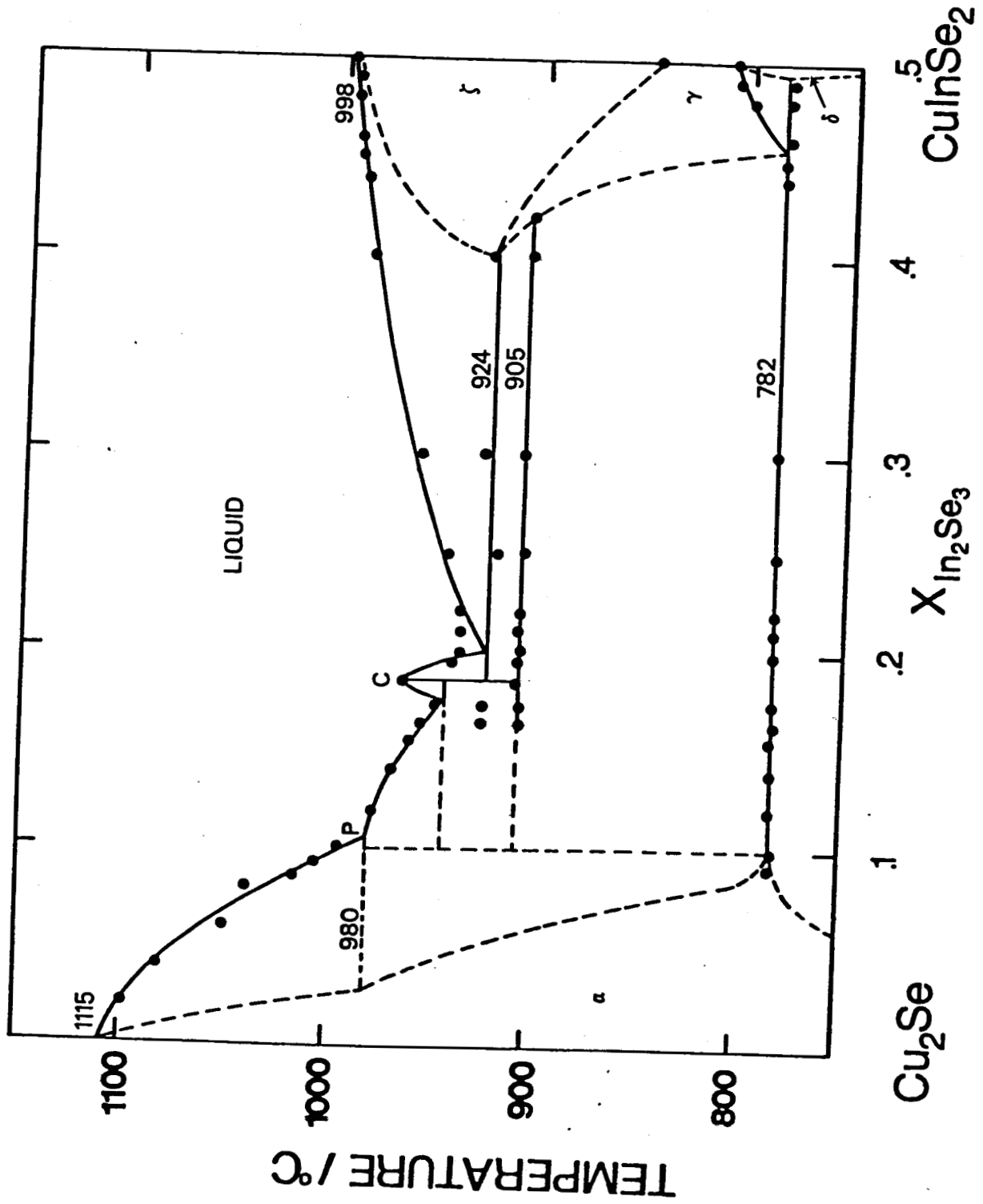


Fig. 14 Pseudobinary cut through the Cu, In, Se Phase Diagram