Submitted to Solid
State Communications

UCRL-20396
Preprint

c.2

BAND ORDERING IN PbTe

Y. W. Tsang and Marvin L. Cohen

December 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UCRL-20396 c.2

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Band Ordering in PbTe*

Y. W. Tsang and Marvin L. Cohen

Department of Physics

and

Inorganic Materials Research Division, Lawrence Radiation Laboratory

University of California, Berkeley, California 94720

*Supported in part by the National Science Foundation

Abstract

Two possible conduction band orderings, I $L_6^-(L_{2'})$, $L_6^-(L_{3'})$, $L_{45}^-(L_{3'})$ and II $L_6^-(L_{3'})$, $L_{45}^-(L_{3'})$, $L_6^-(L_{2'})$ are considered for PbTe using the Empirical Pseudopotential method. Various properties (i. e. optical reflectivity temperature and pressure dependence of the band gap and effective masses) are considered for the two possible orderings.

Bernick and Kleinman[1] recently calculated the energy bands of PbSe, PbS and PbTe by the Lin-Kleinman[2] pseudopotential scheme. They chose pseudopotential parameters to fit the fundamental gaps and some experimental effective masses[3]. They did not, however, fit the optical gaps. Their results were consistent with the experimentally measured effective masses. Such good agreement, however, appears to require that the ordering of the conduction states $L_{3'}^{6^-}$ and $L_{2'}^{6^-}$ be reversed in PbTe from the ordering in PbS and PbSe. That is, whereas the bottom conduction state L_6^- originates from the $L_{2'}$ state (with the removal of spin-orbit interaction from the Hamiltonian) in PbS and PbSe, it originates from the $L_{3'}$ state in PbTe. This ordering is different than that obtained by previous band calculation for PbTe using the APW,[4,5] OPW[6] and EPM[7] methods. These all give the same ordering in PbTe as in PbS and PbSe. The APW method, in addition, gives effective masses[5] in agreement with experiment.

Previous calculations done by the authors, used the Empirical Pseudopotentia method (EPM), concentrating on energy gaps at high energy. These calculations yielded optical properties,[7] fundamental gap temperature dependence[8] and pressure dependence[9] for PbTe in agreement with experiment. However, we were unable to obtain a large mass anisotropy ratio in PbTe; the EPM predictsaa small anisotropy ratio for PbTe. Experimentally determined anisotropy ratios ($K = m_\ell^*/m_t^*$) are 14, 2.0, 1.4 for PbTe, PbSe and PbS respectively.

This work is an attempt to test the results of Bernick and Kleinman, and to compare their results with the results obtained by the EPM calculations. To do sc

we first obtain the Bernick-Kleinman band ordering at L for PbTe using the EPM, then the optical properties, mass anisotropy ratio, temperature dependence and pressure dependence of the fundamental gap derived from the resultant band structure are investigated.

The form factors of the former EPM band structure calculation[7] (hereafter referred to as I) are varied to reverse the ordering of the conduction bands $L_{3'}^{6^-}$ and $L_{2'}^{6^-}$ while keeping the value of the fundamental gap at 0.19 eV. In Fig. 1, the two sets of pseudopotential form factors which give rise to the two different orderings near the gap are shown. The set which gives the Bernick-Kleinman ordering (hereafter called II) is less attractive. The general shape of the band structure throughout the Brillouin Zone derived from both sets of form factors turned out to be similar. The less attractive potential II does raise the two lowest valence bands closer to the gap. Since the interesting structure in the optical spectrum data involves direct transitions mainly within 8 eV of the fundamental gap, the lowest valence bands are too far removed in energy from the gap to contribute to the spectrum. As a result, the imaginary part of the frequency dependent dielectric function, $\epsilon_2(\omega)$, calculated from the band structure (II) does not differ significantly from the one derived from set I.[7] In Table I, the energy levels at L near the fundamental gap calculated from set I and set II of the form factors are tabulated together with the Bernick-Kleinman results and those obtained from APW[4], and OPW[6]

calculations. We note that for the Bernick-Kleinman ordering, the two lowest conduction bands ($L_{3'}^{6^-}$, $L_{3'}^{45^-}$) are spin-orbit split, the large spin-orbit coupling forces the second conduction band to be very close to the third conduction band $L_{2'}^{6^-}$. In the other ordering of conduction states, the spin-orbit splitting occurs between the second and third conduction bands and the above near degeneracy of higher conduction bands does not result.

To determine the effective masses, one may use the $\underset{\sim}{k}\cdot\underset{\sim}{\pi}$ sum rule,

$$\left(\frac{m}{m^*}\right)_{\mu\nu} = \delta_{\mu\nu} + \frac{2}{m}\sum_{\delta}{}' \frac{\langle\gamma|\pi_\mu|\delta\rangle\langle\delta|\pi_\nu|\gamma\rangle}{E_\gamma - E_\delta} , \tag{1}$$

where

$$\underset{\sim}{\pi} = \underset{\sim}{P} + \frac{\hbar}{4mc^2}\,\underset{\sim}{\sigma}\times\underset{\sim}{\nabla V} , \tag{2}$$

$\underset{\sim}{P}$ is the momentum operator, $\underset{\sim}{\sigma}$ the Pauli matrices, V the crystal potential, and γ is the band index for the band of interest. The matrix elements were taken between pseudowavefunctions. Two facts should be commented on for this calculation:

(1) The matrix elements $\langle\delta|\pi_\mu|\gamma\rangle \approx \langle\delta|P_\mu|\gamma\rangle$ are not constant for different bands δ, as was assumed by Dalven[10] in his $\underset{\sim}{k}\cdot\underset{\sim}{P}$ calculation.

(2) The matrix elements $\langle\delta|\pi_\mu|\gamma\rangle$ is large between the top valence band γ and higher conduction bands. Therefore, in spite of the energy difference in the denominator of Eq. (1) and the small fundamental

gap, the contribution $\left(\frac{m}{m^*}\right)_{\mu\nu}$ from the higher conduction bands may not be neglected.

With the EPM, the convergence of the dipole matrix element between pseudowavefunctions is, unfortunately, poor. To determine band energies, a matrix size of about seventy plane waves (including spin) is sufficient to give convergence to 0.1 eV; whereas for the matrix elements, it is necessary to diagonalize an impractically large Hamiltonian matrix to obtain a reliable answer. For this reason, instead of summing the matrix elements in Eq. (1), the Hamiltonian matrix is diagonalized for a few points in k space both $\parallel$ and $\perp$ to the Λ axis very near L; the mass anisotropy ratio is then obtained by curve fitting. An anisotropy ratio $K = m_\ell^*/m_t^*$ of the order of 12.5 is obtained for a carrier concentration of approximately 10^{20} cm^{-3}; K increases for lower carrier concentration. Set I form factors gave $K \approx 1.5$.

Another area of investigation relates to the temperature dependence of the direct gap at L. A recent finite temperature calculation[8] based on the EPM allowed us to obtain both the correct positive sign and the magnitude of the temperature coefficient of the direct gap at L for PbTe. Furthermore, when the form factors 'I of PbTe were scaled to the lattice constant of SnTe, L_6^+ and L_6^- levels at the gap move toward each other and eventually assume a reversed ordering in SnTe. The temperature coefficient of the resultant L gap in SnTe has the correct negative sign. In

this work, a positive gap temperature coefficient is also obtained for PbTe with the form factors II. Fig. 2 presents the $E_g(T)$ curves for PbTe derived from: (a) experiment;[12] (b) our former EPM band structure calculation with form factors I; (c) the present EPM band structure with the Bernick-Kleinman ordering. As can be seen from Fig. 2, the results are consistent with either ordering. This is not too surprising since both have an L_6^+, L_6^- ordering and the mechanism used to explain positive shift in Ref. 8 will be the same in both cases. However, for EPM (II), if the form factors are scaled to the SnTe lattice constant, the valence band (L_6^+) and the conduction band (L_6^-) at the gap move away from each other to give a gap of 0.59 eV. The L_6^+ (valence), L_6^- (conduction) ordering is retained, contrary to the expected 0.3 eV gap with the opposite ordering: L_6^-(valence), L_6^+(conduction) for SnTe.[11]

Lastly, the pressure dependence of the fundamental energy gap $\left.\frac{\partial E_g}{\partial P}\right|_T$ is calculated for both sets of form factors. The energy gap at L is determined for two lattice constants (in this case, they correspond to T = 100 °K and 300 °K). Putting in the experimentally determined compressibility[13], one easily obtains the pressure dependence. From form factor set I, a value of -7.46×10^{-6} eV(bar)$^{-1}$ is derived. This agrees well with the experimentally determined value $-7.4 \pm 0.2 \times 10^{-6}$ eV(bar)$^{-1}$. Form factor set II with the Bernick-Kleinman ordering gives only -3.8×10^{-6} eV(bar)$^{-1}$.

In summary, this work is motivated by the Bernick-Kleinman calculation of the band structure of PbTe, which gives a gap ordering that differs from all other calculations. An attempt was made to "test" the validity of the two different orderings. The criterion of the test is the agreement with experimental measurements of properties that can be extracted from the band structure. The EPM is the basic tool. Our results, however, turn out to be essentially inconclusive. The Bernick-Kleinman ordering gives better masses (non-renormalized for electron-electron or electron-phonon effects), but the "standard" ordering gives a pressure coefficient of the gap which is consistent with experiment, whereas the Bernick-Kleinman ordering does not. We hope this work will encourage new measurements to help determine the correct ordering.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U. S. Atomic Energy Commission.

References

1. R. L. Bernick and L. Kleinman, to be published in Solid State Communications.
2. P. J. Lin and L. Kleinman, Phys. Rev. 142, 478 (1965).
3. K. F. Cuff, M. R. Ellet, C. D. Kuglin, and L. R. Williams, Proc. of the International Conf. on the Phys. of Semiconductors, (Dunod, Paris, 1964), p. 677.
4. J. R. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. 137, A1282 (1965).
5. S. Rabii, Phys. Rev. 167, 801 (1968).
6. F. Herman, R. L, Kortum, I. B. Ortenburg, and J. P. Van Dyke, J. Physique Suppl. 29, C4-62 (1968).
7. Y. W. Tung and M. L. Cohen, Phys. Rev. 180, 823 (1969); M. L. Cohen and Y. W. Tsang, to be published in J. Phys. Chem. Solids.
8. Y. W. Tsang and M. L. Cohen, to be published in Phys. Rev.
9. Y. W. Tung and M. L. Cohen, Physics Letters A29, 236 (1969).
10. R. Dalven, Phys. Rev. Letters 24, 1015 (1970).
11. J. O. Dimmock, I. Melngailis, and A. J. Strauss, Phys. Rev. Letters 16, 1193 (1966).
12. R. N. Tauber, A. A. Machonis, and I. B. Cadoff, J. Appl. Phys. 31, 4855 (1966).
13. B. Houston, R. E. Strakna, and H. S. Belson, J. Appl. Phys. 39, 3913 (1968).

Table Caption

Table I. Energy levels at L near the fundamental gap given by OPW, APW, EPM (I), EPM (II) and Bernick-Kleinman pseudopotential scheme.

Figure Captions

Figure 1 Pseudopotential for PbTe—full curve from EPM (I), dashed curve from EPM (II).

Figure 2 Temperature dependence of fundamental gap in PbTe derived from experiment, EPM (I) and EPM (II). (The experimental data were from Ref. 13).

Table I

Conventional ordering of conduction bands				Bernick-Kleinman ordering of conduction bands		
Energy Level Symmetry	Energy (eV) by OPW method[6]	Energy (eV) by APW method[4]	Energy (eV) by EPM (I)[7]	Energy level Symmetry	Energy (eV) by EPM(II)	Energy (eV) by Bernick-Kleinman[1]
L_{45}^{-} ($L_{3'}$)	1.95	1.66	2.11	L_{6}^{-} ($L_{2'}$)	1.06	1.33
L_{6}^{-} ($L_{3'}$)	1.45	1.06	1.49	L_{45}^{-}($L_{3'}$)	0.98	1.23
L_{6}^{-} ($L_{2'}$)	0.25	0.12	0.19	L_{6}^{-}($L_{3'}$)	0.19	0.19
GAP						
L_{6}^{+}(L_{1})	0	0	0	L_{6}^{+} (L_{1})	0	0
L_{45}^{+} (L_{3})	-0.95	-0.91	-0.98	L_{45}^{+}(L_{3})	-0.92	-0.79
L_{6}^{+} (L_{3})	-1.53	-1.54	-1.97	L_{6}^{+} (L_{3})	-1.54	-1.33

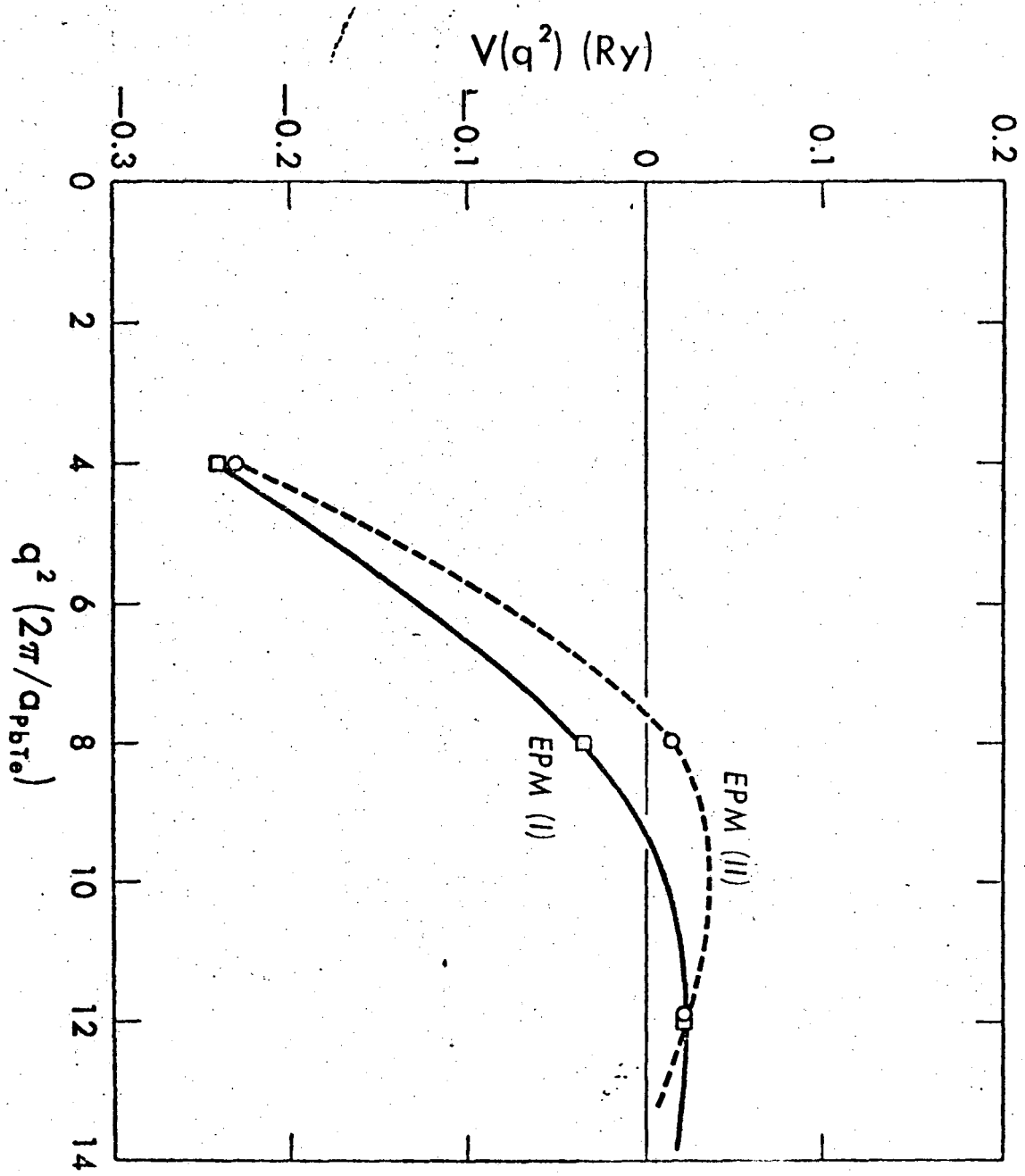

Fig. 1

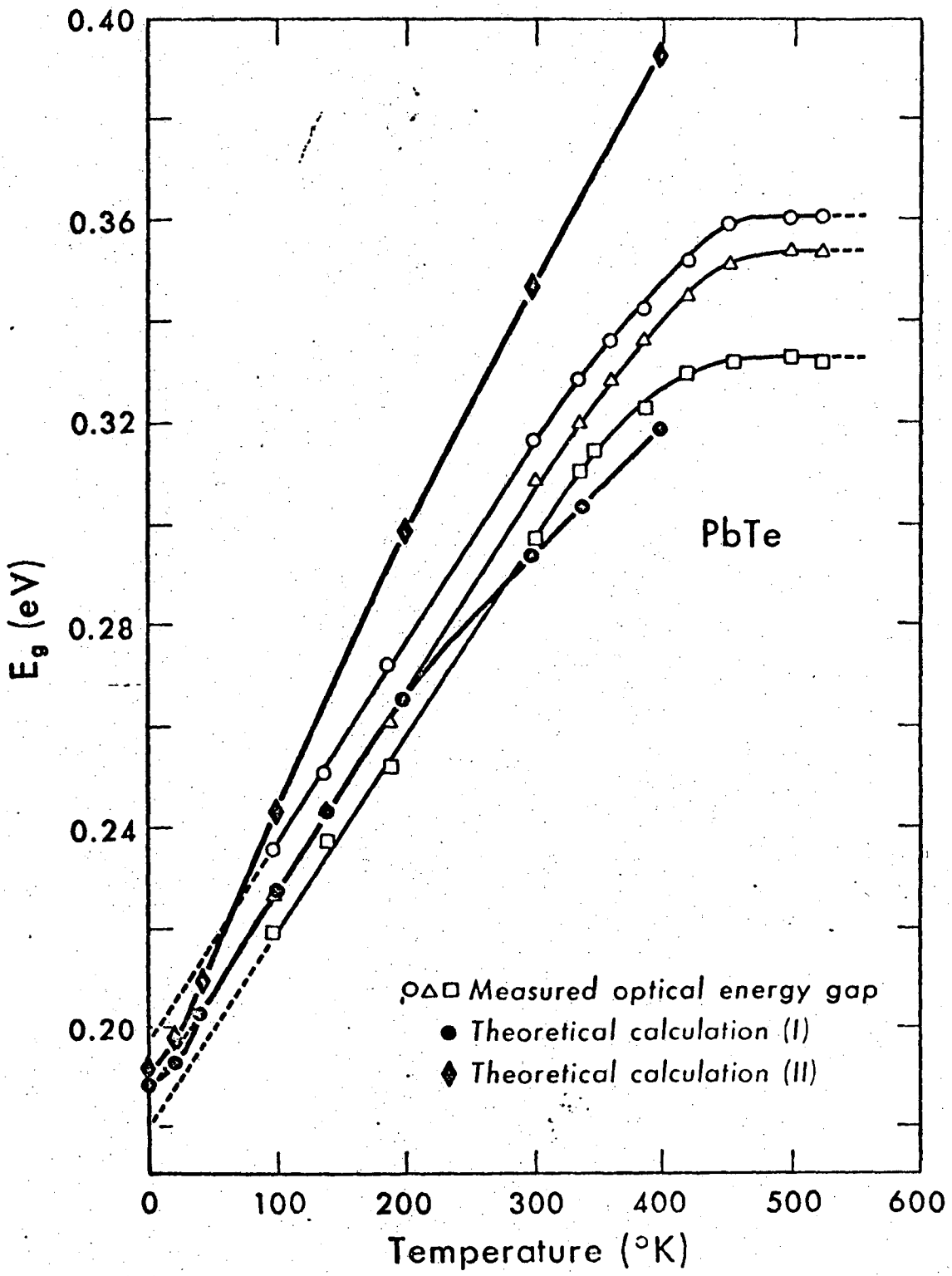
0.40
0.36
0.32
0.28
0.24
0.20
E_g (eV)
PbTe
○△□ Measured optical energy gap
● Theoretical calculation (I)
♦ Theoretical calculation (II)
0
100
200
300
400
500
600
Temperature (°K)

Fig. 2

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720