Title

PSEUDOPOTENTIAL CALCULATIONS OF THE ELECTRONIC STRUCTURE OF A TRANSITION METAL COMPOUND?NIOBIUM NITRIDE

Author

Fong, C.Y.

Publication Date

1972-05-01

Submitted to
Physical Review

LBL-857
Preprint c.1

PSEUDOPOTENTIAL CALCULATIONS OF THE ELECTRONIC STRUCTURE OF A TRANSITION METAL COMPOUND--NIOBIUM NITRIDE

C. Y. Fong and Marvin L. Cohen

May 1972

AEC Contract No. W-7405-eng-48

LBL-857 c.1

Pseudopotential Calculations of the Electronic Structure of a Transition Metal Compound -- Niobium Nitride

C. Y. Fong

Department of Physics, University of California
Davis, California 95616

and

Marvin L. Cohen*

Department of Physics, University of California

and

Inorganic Material Research Division
Lawrence Berkeley Laboratory, Berkeley, California 94720

*Supported by the National Science Foundation under Grant GP 13632.

Abstract

The electronic band structure, density of states, and $\varepsilon_2(\omega)$, the imaginary part of the dielectric constant, are calculated for niobium nitride using the empirical pseudopotential method. The results are compared with non-self-consistent and with the self-consistent APW calculations. A discussion of the Fermi surface is included.

I. Introduction

We have recently developed a scheme[1], which is a simple modification of the usual form of the empirical pseudopotential method[2] (EPM) for simple metals and semiconductors, to calculate the electronic properties of noble metals[3] and a transition metal-niobium[4]. The advantage of this scheme is its simplicity and its flexibility. In the cases of the noble metals and the transition metal, this empirical scheme involves less (8) parameters than previous pseudopotential-tight binding schemes. It is also unnecessary to know a priori the region in the Brillouin zone (BZ) where the hybridization between the s and d electrons is strongest for these crystals. All one needs are the energies at a few high symmetry points inside the BZ and the width of the d-bands. The energies and the width of the d-bands can be determined by optical measurements[3,5] and photoemission experiments[6] respectively. Furthermore, the atomic pseudopotential extracted from one calculation can be used at least as a starting potential for other compounds with the same atom as a constituent[2]. It is this flexibility which enables us to calculate the electronic properties of a series of compounds.

In this report we concentrate on a transition metal compound. This class of compounds is extremely interesting. Some of these compounds are high temperature superconductors, and others exhibit interesting metal-insulator transitions. It is felt that a vast amount of basic knowledge about solids can be obtained through studies of these kinds of crystals, and it is, therefore, necessary to have an effective method to study the electronic properties of these compounds. We have anticipated in Ref. 1 that the EPM can be used for this purpose. Here, we report the first energy band structure of a transition metal compound (niobium nitride) obtained by using the EPM. We would like to make a few comments about the significance of the present calculation:

A. Despite the fact that the band structure presented is fitted to first principles calculations (due to the lack of experimental information) the results indicate that it is now possible to determine with even more accuracy the energy band structure of interesting transition metal compounds if optical and photoemission data are available. B. NbN is a high temperature superconductor with $T = 15.7^{\circ}K$.[7] We anticipate that the pseudopotential derived here for NbN, can be used in the future to study the origin of the high superconducting transition temperature for this compound. Furthermore, if more optical and photoemission data relating to the transition metal compounds are available, one can use the results of the EPM to predict the superconducting transition temperature. C. Experimental studies on NbN, up to present, are restricted to mechanical, electrical and superconducting properties. If optical data were available we could refine our calculation. For the present, we give a calculation of the imaginary part of the dielectric function as a rough prediction of the optical spectrum. D. Earlier theoretical studies were done by Mattheiss[8] (who also summarized results for similar compounds) using the APW method and by Schwarz[9] who used the self-consistent APW method. There exists large discrepancies between the two APW results. As we will show the results of the EPM fits Schwarz's calculations better than Mattheiss' results. This paper will be presented in four sections. In section II, we discuss the method of calculation. The results are given in section III. Finally, section IV presents the summary and conclusions of this study.

II. Method of the Calculation

The general form of the pseudopotential Hamiltonian has the following form:

$$\mathcal{H} = -\frac{\hbar}{2m}\nabla^2 + V_L(\vec{r}) + V_{NL}(\vec{r}) \qquad (1)$$

where $V_L(\vec{r})$ is the local pseudopotential and $V_{NL}(\vec{r})$ is the nonlocal pseudopotential. The potential $V_L(\vec{r})$ is expanded in the reciprocal lattice

$$V_L(\vec{r}) = \sum_{\vec{G}} V(|\vec{G}|)\, e^{i\vec{G}\cdot\vec{r}} \qquad (2)$$

where $\vec{G}$ is a reciprocal lattice vector in units of $(2\pi/a)$, a is the lattice constant and is equal to 4.39 Å.[7] $V(|\vec{G}|)$ is the pseudopotential form factor. We truncate the series at $|\vec{G}|^2 = 12$. NbN has the rocksalt structure; the origin of the coordinate system is taken at the Nb atom and the position of N atom is at $\frac{a}{2}(1,1,1)$. The truncation, then, leaves two antisymmetric form factors, V^A, at $|\vec{G}|^2 = 3$ and 11 and three symmetric form factors, V^S, at $|\vec{G}|^2 = 4,8$ and 12.

$V_{NL}(\vec{r})$ contains two separate parts: A. A d-wave non-local potential to account for the part of the potential for the d-electrons of the Nb atom which is over-cancelled in $V_L(\vec{r})$. The form of this d-like $V_{NL}(\vec{r})$, centered at the Nb atom, is the same as given in Ref. 1 and has the following form:

$$V_{NL}^{\ell=2}(\vec{r}) = \sum_j P_2^{\dagger} V_2 (|\vec{r}-\vec{R}_j|) P_2 \tag{3}$$

where $\vec{R}_j$ is the lattice vector. $P_2^{\dagger}$ and P_2 are projection operators. They project out the $\ell=2$ component of the wavefunctions when the matrix elements of the $V_{NL}^{\ell=2}(\vec{r})$ are calculated over a convenient basis.

$$\begin{aligned} V_2(|\vec{r}-\vec{R}_j|) &= A_2 , \quad \text{for} \quad |\vec{r}-\vec{R}_j| \le R_2 \\ &= 0 , \quad \text{otherwise} \end{aligned} \tag{4}$$

where A_2 and R_2 are treated as disposable parameters. Since we want to obtain good convergence for the energy of the d-band using a plane wave basis, we introduce a damping factor of the form (as in Ref. 1):

$$\langle \vec{k}+\vec{G}| V_{NL}^{\ell=2}(\vec{r}) | \vec{k}+\vec{G}'\rangle \rightarrow e^{-\alpha\{\frac{1}{2k_F}[|\vec{k}+\vec{G}|-\kappa]\}^2} \langle \vec{k}+\vec{G}| V_{NL}^{\ell=2}(\vec{r}) | \vec{k}+\vec{G}'\rangle e^{-\alpha\{\frac{1}{2k_F}[|\vec{k}+\vec{G}'|-\kappa]\}^2} \tag{5}$$

where α and κ are treated as parameters and k_F is taken as the Fermi momentum of Nb.

B. A p-wave non-local potential since the core states of the N-atom is $(1s)^2$ and there is no p-like core states. The valence states $(2s)^2(2p)^3$ have both s an p character. Similar to the case of BN[10] we introduce a nonlocal pseudopotential for the p-electrons. This p-like nonlocal pseudopotential takes the following form

$$V_{NL}^{\ell=1}(\vec{r}) = \sum_j P_1^\dagger V_1 (|\vec{r}-\vec{R}_j-\vec{\tau}|) P_1 \qquad (6)$$

where $P_1^\dagger$ and P_1 are projection operators similar to P_2 but they project out the ℓ=1 component only. $\vec{R}_j$ is the same lattice vector defined above. $\vec{\tau} = \frac{a}{2}(1,1,1)$ so that $V_1(\vec{r})$ is centered around the N-atom in each unit cell.

$$V_1(|\vec{r}|) = A_1 r e^{-\beta r}, \quad \text{for } |\vec{r}| \le R_1 \qquad (7)$$
$$= 0 \qquad \text{otherwise}$$

where A_1 and β are treated as parameters. The value of R_1 is set equal to the ionic radius 0.25 Å[11] of N^+, it is not varied during the fitting process.

The pseudopotential Hamiltonian, then, is diagonalized over plane wave basis states. In order to obtain convergence for the energies at Γ, X and L to within 0.1 eV, we use E_1 = 20.1 and E_2 = 40.1 in units of $(2\pi/a)^2$, the size of the matrix is of the order of 100 x 100 and there are about 175 plane waves contributing to the Löwdin-Brust perturbation[12].

III. Results

Because of the lack of optical and photoemission data for NbN, we decided to use the APW results to obtain values for the parameters in our theory. We started by extracting the N potential from BN. We then scaled both the extracted N potential and the Nb potential to the lattice constant of NbN. These scaled potentials/then are adjusted to fit the energies obtained by the first principles band calculations. We first tried to fit the results obtained by Mattheiss as we had done for Nb with the hope that a consistent Nb pseudopotential usable for both materials might be obtained. However, we obtained a reversal in the order of the L_3 and L_1 states for the valence bands. It was impossible to reverse this ordering without giving up the agreement obtained for the energy gaps at Γ and X. We found that further variation gave results similar to the self-consistent APW results by Schwarz[9] and we then used this calculation to obtain our parameters. The ordering of the L_3 and L_1 states was still the main difficulty. We finally managed to obtain the same ordering as in Ref. 9, by sacrificing the agreement of the position of the X_1 band derived from Γ_{12}. The resulting form factors and the parameters relating to the $V_{NL}(\vec{r})$ are listed in Table I. We do not compare these values of the pseudopotential to the scaled ones for two reasons: A. We obtained the Nb results using Mattheiss'[8] results for pure Nb. In this calculation we use the results of Ref. 9, and the results between Refs. 8 and 9 are quite different. Therefore, we do not expect that the Nb potential from the present calculation will be consistent with the one obtained in Ref. 4 and without optical data we cannot decide which one is more accurate. B. The scaled N potential from BN was not expected to be accurate, because only one piece of experimental information is used to determine the potential.

The band structure along various symmetry directions is given in Fig. 1. The best agreement between this calculation and the ones in Ref. 9 is for the Γ point of the BZ. A comparison of a few important energy gaps between the present results and Refs. 8 and 9 is given in Table II. The density of states derived from the band structure is plotted in Fig. 2. The Fermi energy is at 3.3 eV above Γ_{15}. The peak in the density of states for the lower bands is about 0.8 eV lower than the corresponding one in Ref. 9 measured with respect to Γ_{15}. This shows that our bands near K are lower in energy than the APW results. The peak of the density of states for the higher bands is at 4.9 eV above Γ_{15}. The APW results show a peak at 4.4 eV. The general shape and the relative magnitude of the peaks for both results agree quite well. The Fermi surface for bands 5, 6, 7 and 8 are given in Fig. 3. Band 9 is omitted because the Fermi surface for this band is a very small pocket centered around Γ (from the Γ_{12} level). Except for band 6, the shape of the bands are very similar to the ones in Ref. 9. For band 6, the bending of X_1 gives a small pocket near X. One plausible reason for the bending of X_1 is due to the hybridization. As we mentioned in Ref. 4, the pseudopotential results for Nb showed stronger hybridization than the APW results. Here, the hybridization is evident for the two Δ_1 bands, and it causes a lowering in energy of the band X_1. In order to provide some information about the optical properties of NbN and to stimulate experimental work, we give the joint density of states and ε_2, the imaginary part of dielectric constant due to interband transitions only, with dipole matrix elements calculated by using pseudowavefunctions in Figs. 3 and 4. The peak at 0.1 eV in both the joint density of states and $\varepsilon_2(\omega)$ is due to $6 \rightarrow 7$ transitions. However, the structure in ε_2 at 0.6 eV is from $5 \rightarrow 6$ transitions. This structure is caused by the matrix elements calculated in the pseudowavefunctions approximation.

IV. Conclusion

We have presented preliminary results for NbN using the empirical pseudopotential method. The energies were fitted to a self-consistent APW result by Schwarz[9]. The general agreement can be considered to be consistent to within approximately 0.5 eV. The main purpose of this calculation is to show that the empirical pseudopotential method can now be applied to transition metal compounds. In the future, when optical data becomes available, systematic studies on these compounds can become feasible, and we expect that one can improve on the results presented here for NbN.

Acknowledgment

We would like to thank Dr. L. F. Mattheiss for sending us his results before the publication and several helpful conversations. Part of this work was done under the auspices of the United States Atomic Energy Commission.

References

1. C. Y. Fong and M. L. Cohen, Phys. Rev. Letters 24, 306 (1970).
2. M. L. Cohen and V. Heine, Solid State Physics 24 (Academic Press, Inc., New York, N. Y. 1970), p. 37.
3. C. Y. Fong, M.L. Cohen, R. R. L. Zucca, J. Stokes and Y. R. Shen, Phys. Rev. Letters 25, 1486 (1970); J. Stokes, Y. R. Shen, Y. W. Tsang, M. L. Cohen and C. Y. Fong, Phys. Letters 38A, 347 (1972).
4. C. Y. Fong and M. L. Cohen, (to be published).
5. For example, U. Gerhardt, Phys. Rev. 172,651 (1968).
6. For example, N. V. Smith, Phys. Rev. B3, 1862 (1971).
7. T. H. Geballe, B. T. Matthias, J. P. Remeika, A. M. Clogston, V. B. Compton, J. P. Maita and H. J. Williams, Physics 2, 293 (1966).
8. L. F. Mattheiss, Phys. Rev. B5, 315 (1972).
9. K. Schwarz, Monatsh. Für Chem. 102, 1400 (1972).
10. L. A. Hemstreet, Jr. and C. Y. Fong, (submitted to Phys. Rev.).
11. L. Pauling, "The Nature of the Chemical Bond", 3rd ed. p. 514; Cornell University Press, Ithaca, N. Y. (1960).
12. D. Brust, Phys. Rev. 134, A1337 (1964).

Table Captions

Table I. Parameters for the pseudopotential for NbN.

Table II. Comparison of important energy gaps obtained from EPM and APW calculations.

Figure Captions

Figure 1. Energy band structure of NbN.

Figure 2. Density of states of NbN.

Figure 3a. The shape of the Fermi surface for band 5.

Figure 3b. The shape of the Fermi surface for band 6.

Figure 3c. The shape of the Fermi surface for band 7.

Figure 3d. The shape of the Fermi surface for band 8.

Figure 4a. The joint density of states of NbN. (This is the same as the imaginary part of the dielectric function with constant matrix elements.)

Figure 4b. The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, of NbN with dipole matrix elements calculated from pseudowave functions.

Table I

Parameters for Local pseudopotential	Parameters for Nonlocal d pseudopotential	Parameters for Nonlocal p-pseudopotential
$V^A(\|\vec{G}\|^2 = 3(\frac{2\pi}{a})^2) = 0.4442$ Ry	$R_s = 1.18$ Å	$V_p^{NL} = A_1 r e^{-\alpha r}$ $r \le R_p$
$V^A(11) = 0.0600$	$\alpha = 0.118$	$R_p = 0.25$ Å
$V^S(4) = -0.1812$	$\kappa = 1.73\ (\frac{2\pi}{a})$	$\alpha = 1.15$ Å^{-1}
$V^S(8) = -0.1411$	$A_2 = -4.8624$ Ry.	$A_1 = -0.67$ Ry./Å
$V^S(12) = -0.0661$	$a = 4.39$ Å	

Table II

Energy gaps / Symmetry / Authors	K. Schwarz (APW self-consistent)	L. F. Mattheiss (APW)	Fong - Cohen (EPM)
$\Gamma_1 \rightarrow \Gamma_{15}$ (s-p)	6.54 eV.	9.67 eV.	6.52 eV.
$X_4' \rightarrow \Gamma_{15}$ (p-p)	2.39	1.2	2.25
$X_5' \rightarrow \Gamma_{15}$ (p-p)	0.6	0.38	0.9
$\Gamma_{15} \rightarrow \Gamma_{25}'$ (p-d)	1.14	5.24	1.14
$\Gamma_{15} \rightarrow \Gamma_{12}$	3.11	7.08	3.14
$L_1 \rightarrow \Gamma_{15}$	5.67	3.58	4.84
$L_3 \rightarrow \Gamma_{15}$	3.51	2.22	4.21
$X_3 \rightarrow \Gamma_{15}$	2.01	-2.27	1.74
$\Gamma_{15} \rightarrow X_1$	6.94	10.09	2.68

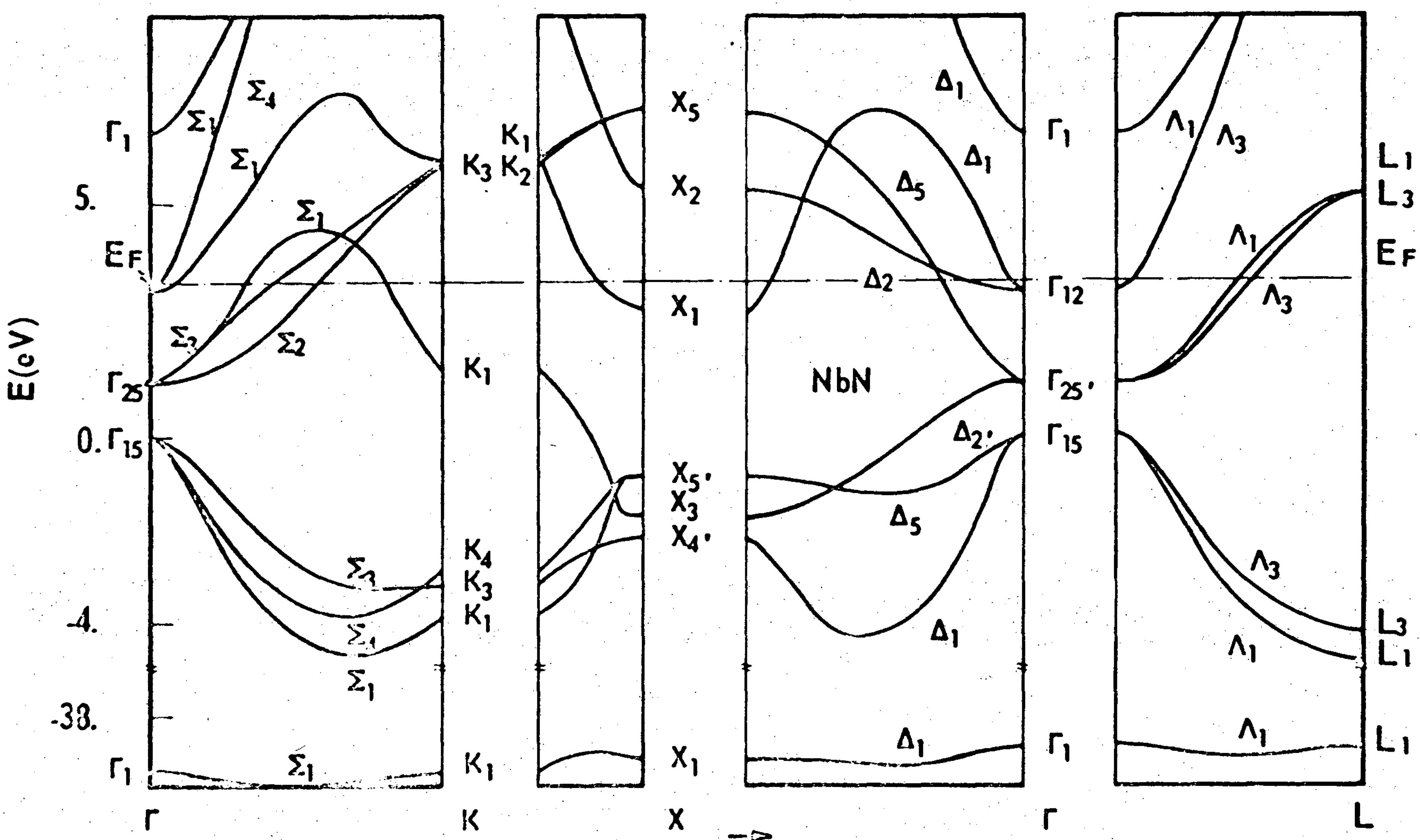

Fig. 1

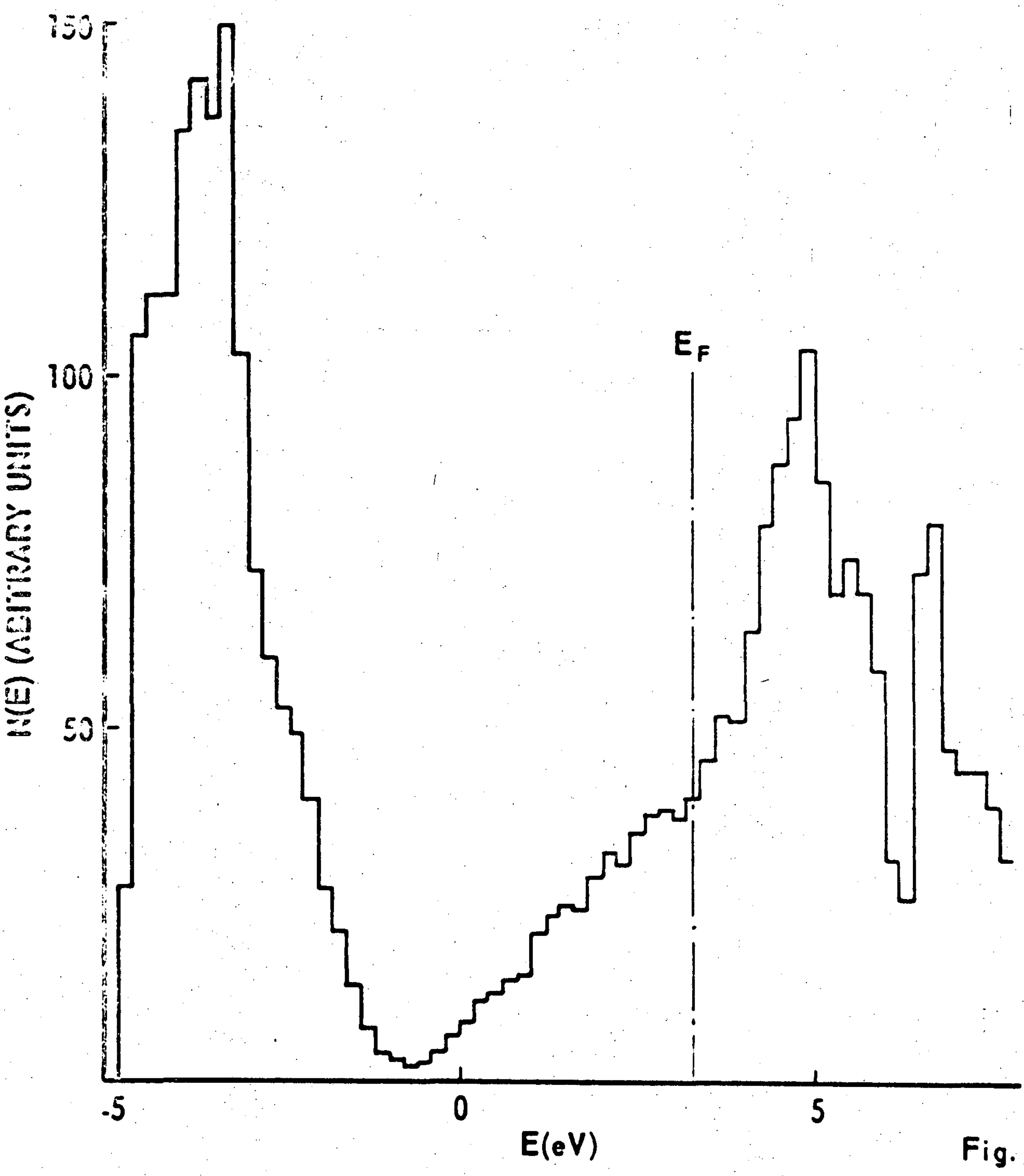

Fig. 2

5 Band

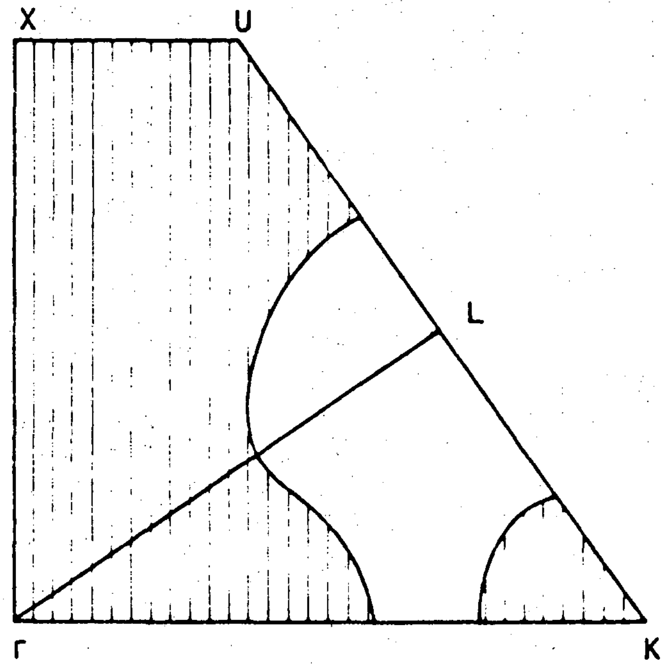

Fig. 3a

6 Band

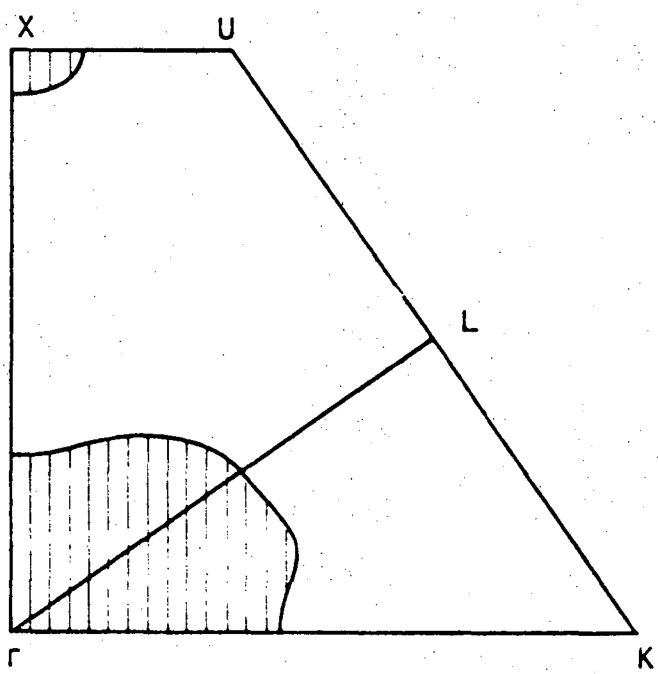

Fig. 3b

7 Band

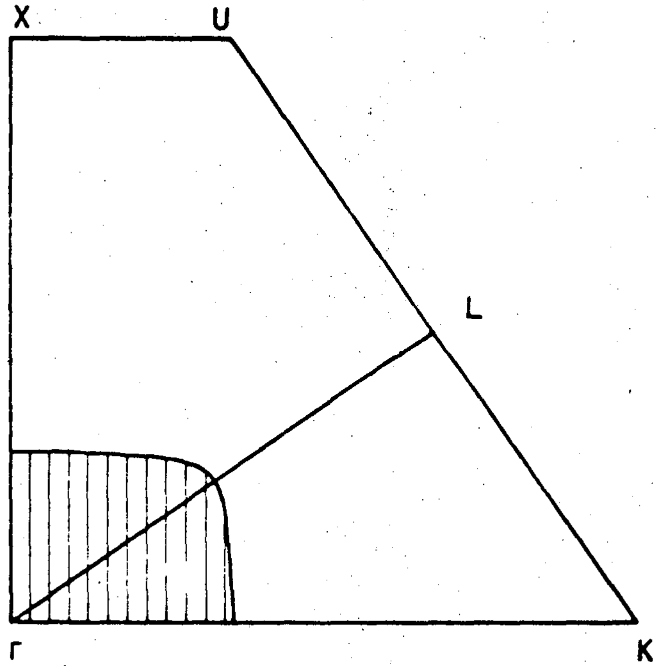

Fig. 3c

8 Band

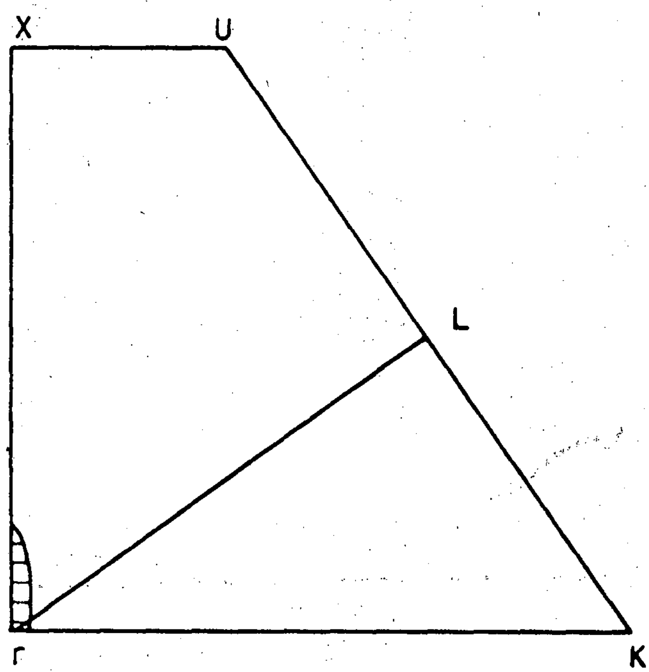

Fig. 3d

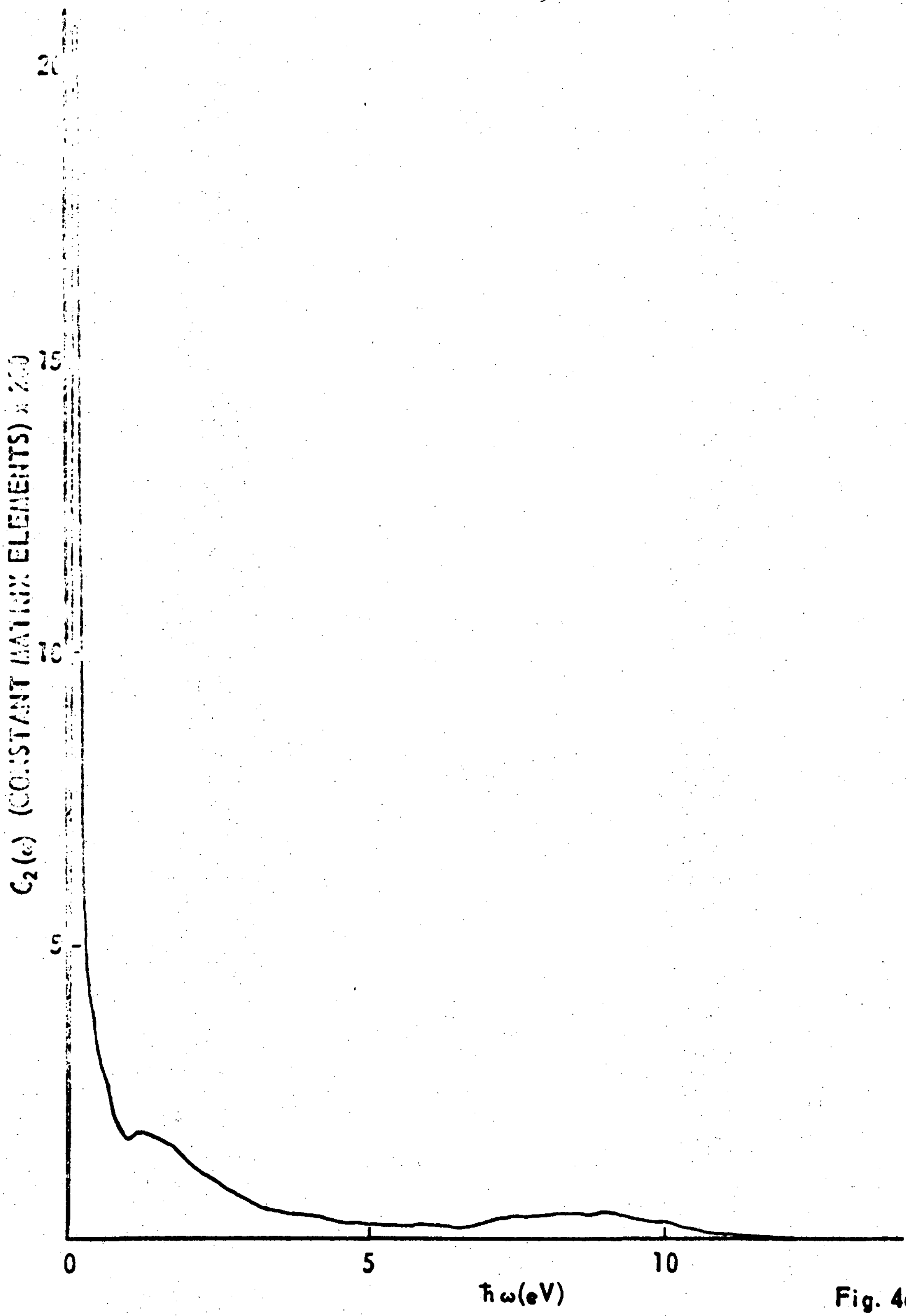

Fig. 4a

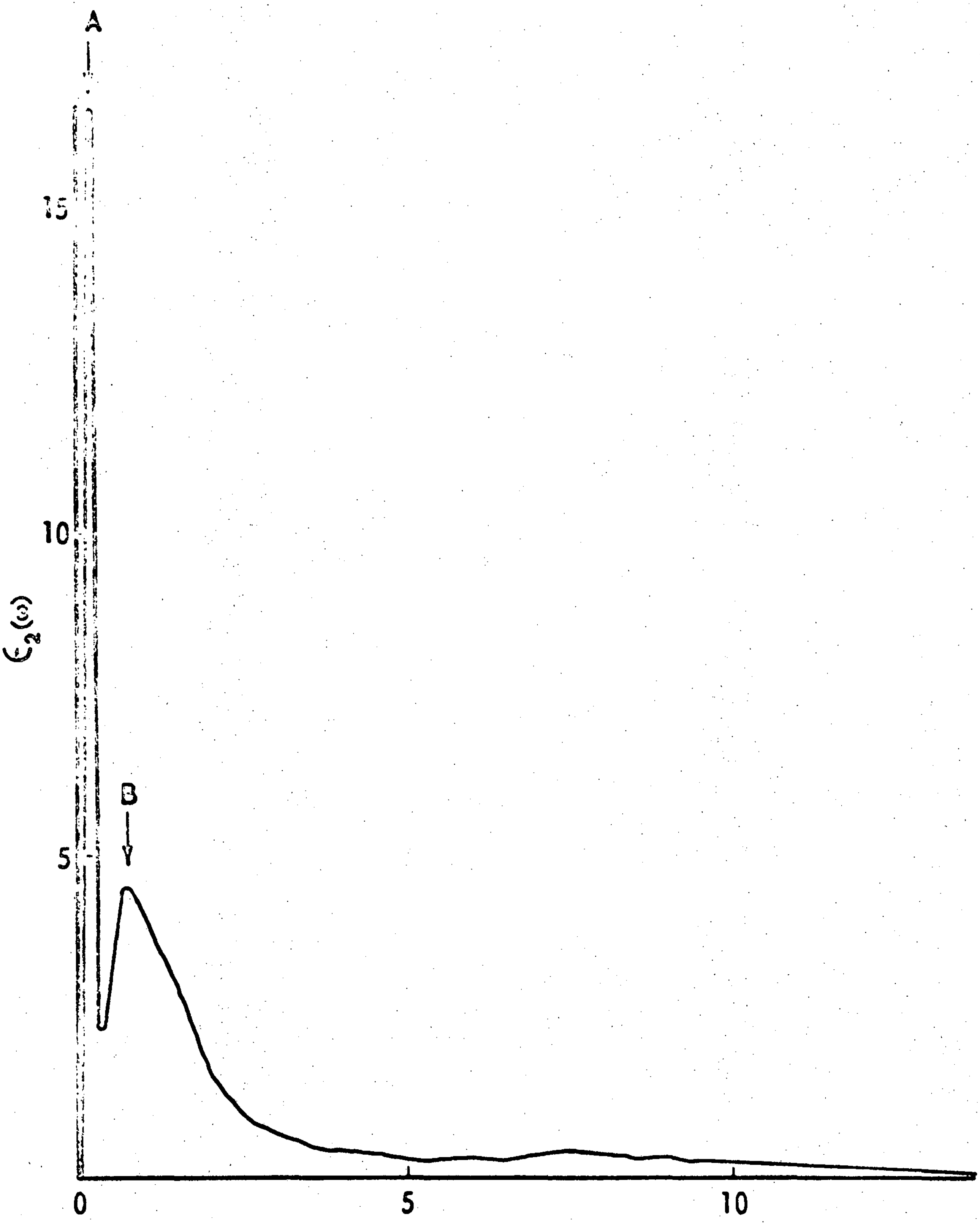

Fig. 4b

U U U U U 8 U 1 U 1 7

LEGAL NOTICE

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