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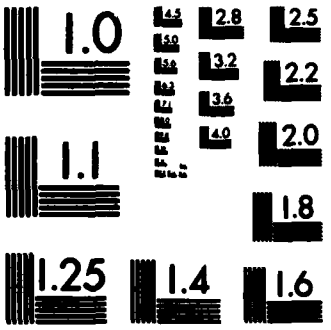

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N00014-80-K-0852

Task No. 056-681

Technical Report No. 13

UNDERSTANDING LOCALIZED BEHAVIOR IN THE AUGER SPECTRA OF COVALENT SYSTEMS SUCH AS GRAPHITE

By

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Prepared for Publication

in

Journal of Vacuum Science and Technology

George Washington University
Department of Chemistry
Washington, D.C. 20052

September 1983

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: No. 13	2. GOVT ACCESSION NO. AD-A133 924
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): UNDERSTANDING LOCALIZED BEHAVIOR IN THE AUGER SPECTRA OF COVALENT SYSTEMS SUCH AS GRAPHITE.	5. TYPE OF REPORT & PERIOD COVERED: Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): D. E. Ramaker, F. L. Hutson, R. R. Rye, J. E. Houston, and J. W. Rogers	8. CONTRACT OR GRANT NUMBER(s): N00014-80-K-0852
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Chemistry Department, George Washington University, Washington, D.C. 20052	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Prog. Elem. No. 61153N, Task Area No. PP 013-08-01, Work Unit # NR 056-681
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Dept. of Navy, 800 N. Quincy Street, Washington, D.C. 22217	12. REPORT DATE: Sept. 1983
	13. NUMBER OF PAGES: 11
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted for publication in the Journal of Vacuum Science and Technology.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Auger electron spectroscopy, graphite, localization, electron screening.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Localized behavior in the CVV Auger lineshapes of atomic and metallic systems are easily understood within the Cini-Sawatsky theory, which assumes the final state holes are either localized in a single atomic orbital or not at all. In covalently bonded systems, intermediate levels of localization may occur such as onto bond or group orbitals. A set criteria to determine the level of localization has been published, however, a general procedure for determining the distortion effects due to intermediate localization has not been reported. This work describes and justifies the use of the Cini expression on various sub-bands

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of the self fold of the DOS. Application is made to the Auger lineshape of graphite. Although complete delocalization has been indicated for graphite, a reinvestigation of the experimental lineshape, and comparison with a more complete theoretical lineshape, indicates partial localization of the holes in the σ group orbitals and none in the π orbitals. This interpretation is consistent with results for ethylene and benzene.

Understanding Localized Behavior in The Auger Spectra of Covalent Systems Such as Graphite

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Auger core-valence-valence (CVV) lineshapes are often interpreted by comparison to the self-convolution of the valence band DOS, N(E)*N(E). Differences between N(E)*N(E) and the actual lineshape have previously been attributed to localization of the final state holes onto specific orbitals. For instance, the theory of Cini-Sawatzky[1] has been succeessfully applied to atomic-like systems such as the M_1VV lineshape of Cu[2] where only single bands are important in determining the lineshape. In this paper we extend the use of this theory to individual sub-bands of covalently bonded molecular solids in order to interpret the C(KVV) lineshape of graphite.

In previous work, Dunlap et al.[3] provided criteria for assessing the nature of localization in covalent systems onto atomic, bond, group, or extended band orbitals (AO, BO, GO, EBO). These criteria for localization can be summarized as follows:

$$\begin{aligned} &\text{AO:} && V < U_{xx} - U_{xx'} = \Delta U_{xx} \\ &\text{BO:} && V > \Delta U_{xx}\,, \quad \gamma < U_{bb} - U_{bb'} = \Delta U_{bb} \\ &\text{GO:} && \gamma > \Delta U_{bb}\,, \quad \Gamma < U_{gg} - U_{gg'} = \Delta U_{gg} \\ &\text{EBO:} && \Gamma > \Delta U_{gg}\,. \end{aligned} \qquad 1)$$

Here V is the covalent interaction between nearest neighbor carbon AO's and can be estimated from the bonding-antibonding orbital energy separation. γ is the covalent interaction between nearest neighbor BO's and can be estimated from the s and p atomic orbital energy separation. Γ is the covalent interaction between neighboring GO's; in graphite for example the GO's are the planar arrangement of 3 σ or π BO's about a single C atom. U_{xx}, U_{bb}, and U_{gg} are the effective Coulomb interactions between holes localized on a single AO, BO, or GO respectively.

The distortion of the N(E)*N(E) lineshape can be obtained by application of the Cini-Sawatsky[1] theory,

$$A(E) = \frac{[N(E)*N(E)]^2}{[1 - U\,I(E)]^2 + \pi^2 U^2 [N(E)*N(E)]^2}\,, \qquad 2)$$

to individual sub-bands of the DOS. Here U is the effective hole-hole

Coulomb repulsion and I(E) is the Hilbert transform defined as

$$I(E) = \int [N(E)*N(E)]/(E- \varepsilon)d\varepsilon \ . \qquad 3)$$

Fig. 1, utilizing a schematic one-electron DOS, illustrates the validity of this approach. N(E)*N(E) in Fig 1b is representative of the Auger lineshape provided the s, s*, p, and p* bands are all filled and all localization effects are negligible, i.e. $U \equiv \Delta U_{xx} \simeq 0$. Figs. 1c-f show clearly that the distortion effects on each sub-band are reasonably independent of the other regions of the spectrum until U is sufficiently large to encompass these other regions. For U = 0.0 - 1.5, no significant distortion effects occur indicating the EBO's best describe the final state holes. For U = 1.5 - 2.5, the various $\ell\ell'$ (i.e. $\ell\ell$ = ss, sp, etc,) sub-bands are distorted into relatively narrower resonance-like features indicating localization onto single GO's. U = 2.5 - 4 causes the first mixing of bands with different local symmetry (s or p) and indicates localization onto the individual B.O.'s. U = 4 - 15 causes mixing of bands with bonding-antibonding character and indicates localization onto hybrid sp^n atomic orbitals (HO's).

The C(KVV) lineshape for graphite was first reported by Smith and Levinson[4]. An attempt to quantitatively interpret this lineshape has recently been reported by Murday et al[5]. They deduced the one-electron DOS (s, p_σ , π) for graphite from x-ray emission and photoemission spectra and an assumed electron configuration of $sp^2_\sigma \pi$. The Auger lineshape was then produced from a fold of these one-electron DOS assuming complete delocalization, i.e. U = 0. Although Murday et al.

found good agreement between theory and experiment, correction of an error in the post-data acquisition deconvolution procedures of Smith and Levinson[4], as well as an error in the theoretical interpretation by Murday et al.[5], now reveals large descrepancies between the two lineshapes. In particular, a shoulder on the low kinetic energy edge of the experimental lineshape is not reproduced in N(E)*N(E). This descrepancy can be partially eliminated by introducing distortion effects via eq. (2) into the ss, sp_σ , and p_σ p_σ contributions to N(E)*N(E), indicating that partial localization occurs when both holes are in GO's of the σ band, but not when one or both are in the π band.. This interpretation would suggest that electron screening reduces ΔU_{gg} for the π band to a much greater degree than for the σ band. Angular effects, initial core hole screening effects, the accurate removal of "intrinsic" losses from the experimental lineshape, and assumptions made in determining the partial DOS may also be important in fully understanding graphite's C(KVV) lineshape, but an evaluation of these effects will require further detailed study.

This work was supported by the *Office of Naval Research and by the +U.S. Department of Energy under contract # DE-AC04-76DP00789.

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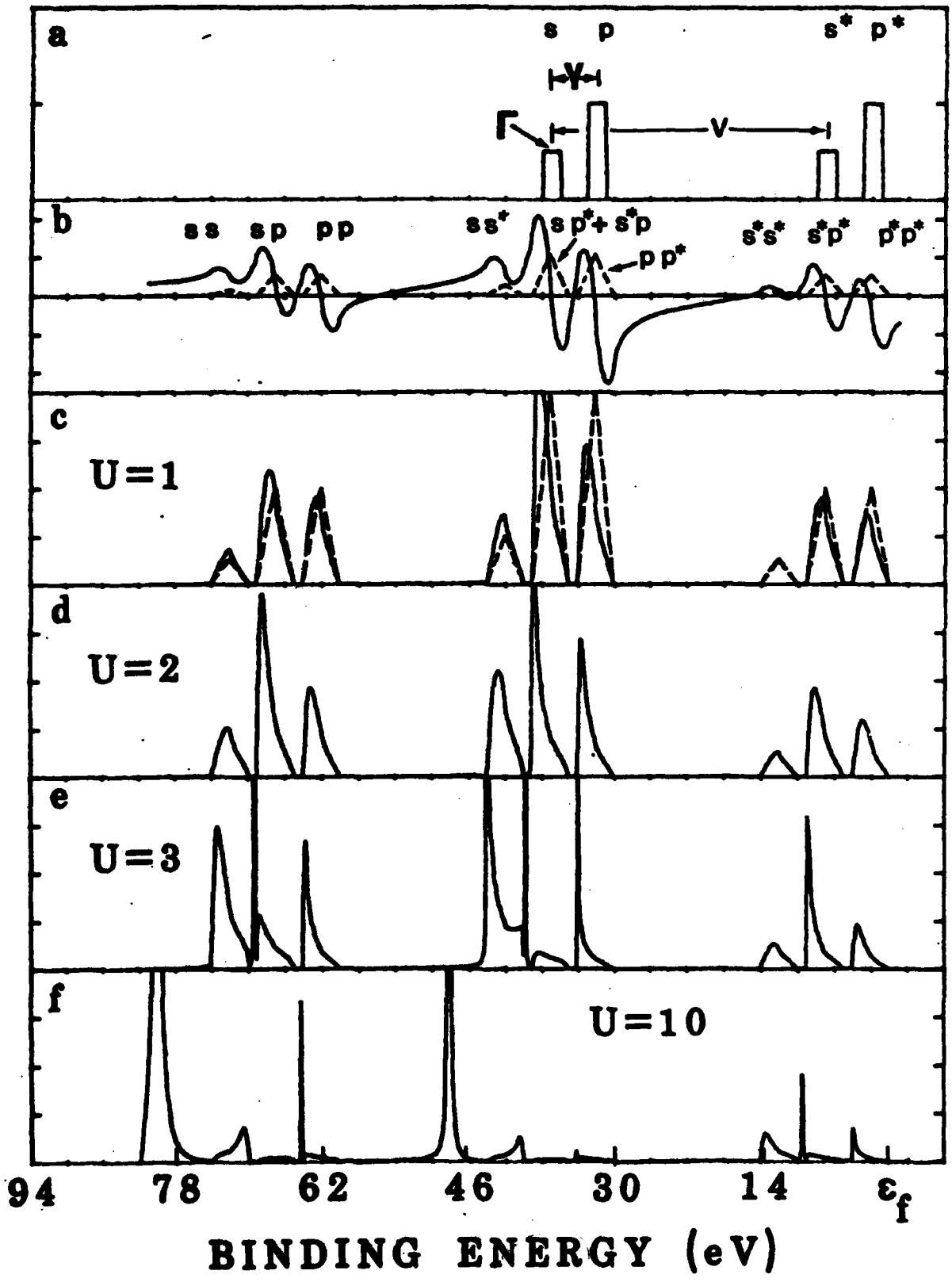
FIGURE CAPTION

a) Schematic one-electron DOS, N(E), illustrating Γ , γ , and V as defined in the text.

b) Self-fold of the one-electron DOS, N(E)*N(E) (dashed line), and the Hilbert transform, I(E) (solid line).

c) Comparison of N(E)*N(E) (dashed line) with A(E) (solid line) obtained from eq. (2) with U = 1 eV.

d-f) A(E) with U = 2, 3, and 10 eV respectively.


a
s p
s* p*
V
Γ
V
b
ss sp pp
ss*
sp*+ s*p
pp*
s*s* s*p* p*p*
c
U=1
d
U=2
e
U=3
f
U=10
94 78 62 46 30 14 εf
BINDING ENERGY (eV)

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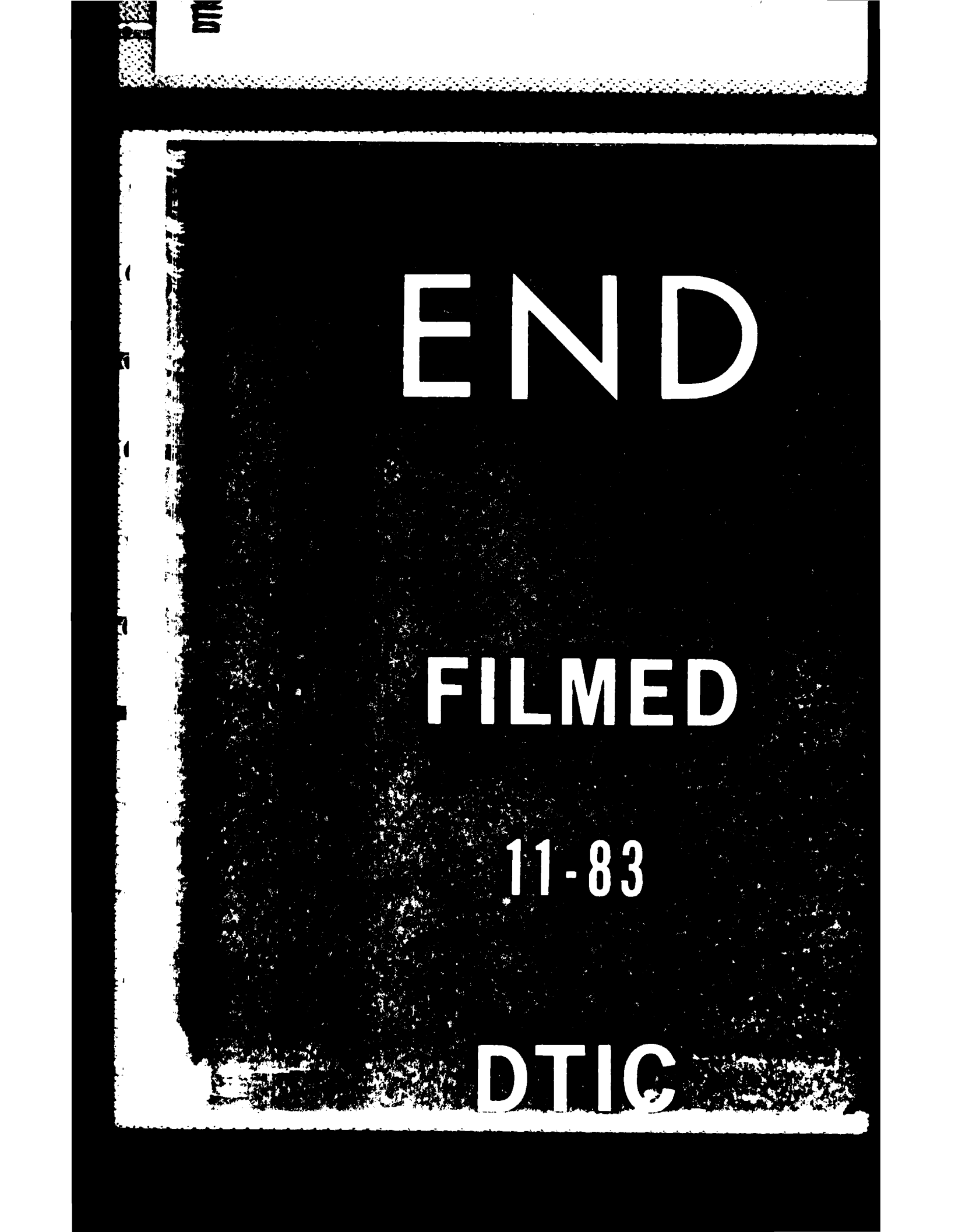
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