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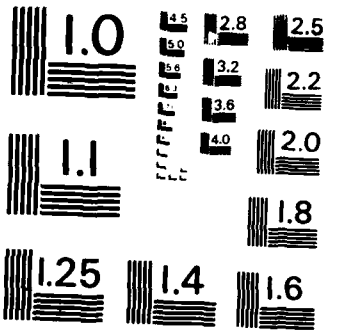

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FINAL REPORT
to the
OFFICE OF NAVAL RESEARCH

Contract Number:	N00014-80-C-0713
Title:	Vibrational Studies of the Structure of Disordered Solids
Principal Investigator:	Frank L. Galeener Xerox Palo Alto Research Center 3333 Coyote Hill Road Palo Alto, CA94304
Period of Contract:	15 July 1980 - 14 March 1984
Budgeted Funds:	$199.1K (for 44 months)

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SUMMARY

The goal of this program was to "further improve our understanding of the vibrational excitations of disordered solids, and to use this knowledge to elucidate the structure of glasses and amorphous thin films". Much significant progress has been made, utilizing Raman, infrared and inelastic neutron scattering experiments, supplemented by novel theoretical work on central force network models and dihedral angle averaged Bethe lattices. Particularly important were the discovery of regular rings of bonds as dominant defects in the otherwise disordered structure of amorphous SiO_2, and the unveiling of simple Raman selection rules for amorphous networks. Twenty two scientific papers have been published, and several more are in the process of completion. The results have excited much interest, as evidenced by the presentation of eleven invited talks on contract work.

Most of the experimental effort was carried out on bulk glasses, including SiO_2, GeO_2, GeS_2, B_2O_3, B_2S_3, BeF_2 and $ZnCl_2$. This was done to develop a fundamental understanding of several network topologies, using materials whose properties are relatively insensitive to details of preparation, and which can be obtained as large samples for neutron scattering. Enough work was done on thin films (SiO_2, Si_3N_4, Nb_2O_5 and Ta_2O_5) to establish the experimental methods for a new study - of *process induced defects* in amorphous insulating films.

The present report includes a list of the published papers, a list of the invited talks and a discussion of the *highlights* of the reported results.

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A. HIGHLIGHTS

The work carried out under contract N00014-80-C-0713 will be described under six headings as follows. (Publications under the contract are listed in the reference section preceded by the letter C.)

I THE THEORY OF VIBRATIONS IN AMORPHOUS NETWORKS

Thorpe and Galeener [C1] generalized the methods of Sen and Thorpe [1] to enable calculation of band limits for the vibrations of amorphous networks with topologies other than the one appropriate for SiO_2. The new method uses coordinate systems which are defined by the covalent bond directions at every individual atom, and thus avoids the coordinate rotations that would otherwise be required in treating a glass with respect to a laboratory frame of reference. The overdetermination that often results is handled easily by a Lagrangian mechanics formulation. The central role of the connectivity matrix of the network is revealed. Expressions for band limits are obtained for numerous topologies, and experiments have been carried out on several examples. This paper provides the framework for treating other topologies and for adding refinements such as non-central forces and long-range coulomb forces.

Galeener and Thorpe [C20] next extended this work to treat networks involving small regular rings of bonds, like those in v-B_2O_3. In particular, band limit formulas were obtained for an A_2X_3 network consisting of regular puckered six-membered A_3X_3 rings. For the special case of planar "boroxol" rings in v-B_2O_3, this theory shows much improved agreement with experiment over a model not containing rings. The remaining discrepancies illustrate the need to include non-central forces in the network dynamics of rings. This paper demonstrated, for the first time, how increased intermediate range order (in the form of regular rings) gives rise to new features in the vibrational density of states of a glassy network.

Barrio, Galeener and Martinez [C22] have used insight gained from this work to develop a new scheme for including non-central forces. It appears that one cannot obtain band edge limits in the simple algebraic form of [C1] and [C20], but one can develop relatively simple computer techniques for calculating the vibrational density of states (VDOS) of an infinite

network having "arbitrary" homogeneous topology. The problem is made "simple" by performing an analytical average over the dihedral angles $\{\phi_i\}$ in the network on the assumption that the ϕ_i are random and uncorrelated. The resultant "ϕ-averaged Bethe lattice" provides a very good fit to the Raman spectra of v-SiO_2 and v-GeO_2 (including non-central forces) and is being exploited to treat network and defect vibrations in other amorphous solids. We believe this will be a particularly valuable tool for treating the vibrations of defects in amorphous solids.

Payne and Inkson [2] have very recently used results from [C1] in order to incorporate the coulomb forces that are required to explain the TO-LO splittings reported [3] in v-SiO_2 and v-GeO_2. At least two other groups are working on related treatments of the TO-LO problem.

Much of this was reviewed in an article by Galeener entitled "Phonons in Glasses" [C9].

II VIBRATIONAL SELECTION RULES IN AMORPHOUS SOLIDS

The only way to determine empirically the vibrational selection rules in a disordered solid is to measure directly (if possible) the vibrational density of states (VDOS), then see which probes (Raman, ir, tunneling spectroscopy, etc.) respond strongly to particular features in the VDOS. Galeener et al. [C3], have obtained a good measure of the VDOS of v-$ZnCl_2$ from measurement of the inelastic neutron scattering spectrum, and compared it with the polarized Raman spectra that were measured. Galeener, Leadbetter and Stringfellow [C16] have made a much more complete study of v-SiO_2, v-GeO_2 and v-BeF_2. They find that the HV Raman spectrum mimics the VDOS but the HH spectrum does not, indicating the presence of strong frequency-dependent matrix elements in the HH Raman response. This corroborates the idea that the HH Raman spectrum selects out a relatively small number of states having a very special SS (symmetric stretch) symmetry, as first predicted in Ref. 4. If these results can be shown to be general, they will be of considerable practical importance in the study of amorphous thin films where inelastic neutron scattering is extremely difficult compared to Raman scattering. In one effort to test generality, inelastic neutron scattering experiments have been planned (with collaborators) on amorphous solids having other topologies, like v-B_2O_3.

Some aspects of generality have been tested by theoretical work, as follows. Martin and Galeener [C4] have applied the Wolkenstein bond polarizability model to the central force model for vibrations in SiO_2-like glasses [1, C1] and successfully interpreted the aforementioned empirical selection rules. The dominant Raman line in the HH spectrum is shown to be due to in-phase motion of the bridging oxygen atoms along the bisector of the angle they subtend with their two nearest neighbours. This strong result was extended by Galeener [C7] to other glass topologies, and has been applied to interpretation of anomalous features such as the sharp "defect" lines seen in the HH Raman spectrum of v-SiO_2 [C8, C11]. Martin and Galeener [C4] were able to give a heuristic argument why the HV Raman spectrum should mimic the VDOS, but this empirical observation has not yet been *proven* mathematically.

Various aspects of the work on vibrational selection rules have been discussed by Galeener in a short review article entitled "Raman Studies of Glass Structure" [C10] and in a more extensive review, "Vibrational Probes of Glass Structure" [C12].

III THE EFFECTS OF ISOTOPIC SUBSTITUTION ON AMORPHOUS NETWORK DYNAMICS

Several experiments were carried out involving the complete substitution of one isotope of an element for another isotope. In an isotopic substitution one changes only the masses, leaving the glass structure and force constants (chemistry) unchanged. This provides a crucial test of the theories developed in I (above) and, having validated the vibrational theories, can provide evidence concerning the structure of the glasses studied.

Galeener and Mikkelsen [C6] carried out the first such substitution in v-SiO_2: thick films (~ 10 μm) of amorphous $Si^{18}O_2$ were formed by steam oxidation of Si in $H_2{}^{18}O$, and high S/N polarized Raman spectra were obtained from these films. All of the peaks were observed to shift to lower frequencies with the change to ^{18}O from the natural (lighter) ^{16}O. The shifts of these broad features were well-predicted by the central force continuous random network (CF-CRN) model [1, C1], as applied to SiO_2-like glasses by Galeener [4]. The two sharp "defect" lines were found to shift as though there were little or no Si motion involved in those two modes.

Galeener and Geissberger [C17] performed a high precision test of these results by obtaining the Raman spectra of v-SiO_2 before and after the substitution ^{28}Si-^{30}Si. While the shifts of the other broad lines were still well-predicted by the CF-CRN model, the dominant Raman line was found to have a small discrepancy, which was explained in terms of an effect of disorder which cannot be included in the CF only models of [C1]. The Raman active "defect" lines D_1 and D_2 exhibited *no* Si mass dependence, which greatly restricted the defect structures that can be considered for their origin. It was concluded that the absence of Si motion is inconsistent with all previous (broken-bond and wrong-bond) models for D_1 and D_2, but is consistent with the recent assignment of D_1 and D_2 to modes of highly ordered (planar) rings of bonds [C11]. These rings will be discussed a bit more in Section IV (below).

Galeener, Geissberger, Ogar and Loehman [C10] reported the ^{16}O-^{18}O and ^{70}Ge-^{74}Ge isotope shifts in the Raman spectra of v-GeO_2. The shifts of the broad features compared well with CF-CRN theory, as was the case for v-SiO_2. The narrow "defect" line at 530 cm^{-1} appears to involve no Si motion and was tentatively identified with a regular ring of bonds. The other narrow line, at 345 cm^{-1}, is unique in that it consists largely of Ge motion, for which no satisfactory model has yet been proposed.

To explore the ring hypothesis, Galeener and Geissberger [C13] carried out Raman studies of ^{10}B-^{11}B isotopic substitution in v-B_2O_3, where planar 3-rings are virtually certain to exist. Two modes were found to exhibit no B isotope shifts. The broad one at 450 cm^{-1} was assigned to the SS of oxygen atoms bridging *between* rings, while the sharp one at 808 cm^{-1} is widely believed to be due to a SS breathing mode of the boroxol ring. This work showed empirically that the signature of a regular ring embedded in an otherwise amorphous network is the existence of an isolated, sharp, highly polarized line which shows little or no cation (B) isotope shift. This has served to strengthen the earlier assignment of the D_1 and D_2 lines to regular rings in v-SiO_2 [C8, C11].

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IV INTERMEDIATE RANGE ORDER IN GLASSES

Much of the work described in I and II (above) enabled explanation of the dominant broad features seen in the Raman and infrared spectra of several glasses in terms of the short range order or nearest neighbour environment of the glass. But short range order alone proved incapable of explaining the sharper features observed in such glasses as v-SiO_2 [4]. v-B_2O_3 [5] and v-As_2O_3 [6]. Galeener [C8, C11] has proposed that these sharp lines are evidence for intermediate range order, in the form of regular (often planar) rings of bonds. An energy minimization argument was devised which predicts that very small rings of bonds are *expected* to be planar (and therefore regular) even when they are embedded in an otherwise disordered network. On this basis, the 606 cm^{-1} D_2 "defect" Raman line in v-SiO_2 was assigned [C8] to the existence of ~ 1% of planar hexagon-like (3-fold) rings. It was also shown that planar 2-fold rings (edge sharing tetrahedra) required too much energy for formation, and this was also the case for cage-like structures (face sharing tetrahedra; adamantane-cages).

The energy minimization argument was refined in a subsequent paper by Galeener [C11], where it was concluded that the D_1 = 495 cm^{-1} line was very probably due to a regular but slightly puckered 4-ring. The D_1 and D_2 frequencies were shown to correspond nicely to breathing modes of 4-rings and 3-rings, respectively, which have been observed in cyclo-silicate minerals [C11] and in cyclo-siloxane molecules [C14]. In [C11], larger concentrations of regular rings (of specific orders) were predicted in numerous other glasses including v-BeF_2, v-GeO_2, v-$GeSe_2$ and v-As_2O_3. Empirical evidence in support of these predictions is growing.

The theoretical work of Galeener and Thorpe [C20] mentioned in Section I (above) is a first effort to understand the dynamics of the atoms in regular rings embedded in a disordered host network. Moderate success was achieved in understanding the ^{10}B-^{11}B isotope shifts reported in [C13], and the discrepancies were confidently ascribed to the lack of non-central forces. This means that proper treatment of the regular rings requires inclusion of both central and non-central forces in the problem.

Geissberger and Galeener [C15] have extended the ring studies to a previously unsynthesized glass, v-B_2S_3. by comparison of the Raman spectra of this glass with those of a known crystalline form, they concluded that the glass contains both 2-fold and 3-fold planar rings of B-S bonds. This was the first known case of 2-fold rings in a glass; however, similar 2-rings have now been reported in v-SiS_2 [7].

Much of the work concerning regular rings in glasses has been discussed in a review by Galeener, entitled "Vibrational Evidence for Intermediate Range Order in Glasses" [C14].

V APPLICATIONS OF VIBRATIONAL SPECTROSCOPY TO GLASS SCIENCE

These activities have in common the development of Raman spectroscopy as a monitor for the effects of various aspects of environment (or sample history) on the properties of v-SiO_2.

It was pointed out quite some time ago by Galeener and Geils [8] that the strongly polarized well-isolated Raman line seen in vitreous SiO_2 at 3700 cm^{-1} could be used to accurately measure "water" concentration in fused silica. Exploiting this, Galeener and Mikkelsen [C5] have developed non-destructive techniques which enable the profiling of OH in fused silica. Spatial resolution of ~ 50 μm was achieved, and order-of-magnitude improvements were confidently predicted. It is likely that some other diffused impurities can be profiled this way, and there would seem to be applications for the study of weathering, corrosion, etc. The results of [C5] have recently been used in Great Britain by groups concerned with the degradation of undersea fibre optic cables [9].

Geissberger and Galeener [C18] have completed a detailed study of the Raman spectra of v-SiO_2 as a function of sample fictive temperature T_F for 900°C $\leq T_F \leq$1550°C. These observations were made: (1) the broad features (network lines) change frequency in a manner consistent with densification by reduction of the average Si-O-Si angle θ; (2) the sharp "defect" lines D_1 and D_2 show little or no shift in frequency; (3) both defect line intensities exhibit Arrhenius behaviour, $\exp(-\Delta E/k_B T_F)$, with well-defined activation energies ΔE of 0.14 and 0.40 eV respectively. It was found that these observations do not change with OH concentration, but that the rate of relaxation of structure at a new annealing temperature depends strongly on

temperature and on the OH concentration. These observations contain more information about the network and defect structure of v-SiO_2 (as well as structural relaxation processes) than we presently know how to understand. Nevertheless, the behaviour of the D_1 and D_2 lines is completely consistent with the ring models introduced in [C8] and [C11].

Galeener, Geissberger and Weeks [C21] have utilized the information obtained above [C18] to gain insight into the geological origin of Libyan Desert glass (LDG), which is about 98% pure SiO_2. LDG shows polarized Raman spectra that are virtually identical to those of pure v-SiO_2. The time-temperature dependence of the D_2 "defect" lines in LDG was studied and then used to infer information about the thermal history of a pristine sample of the natural glass. It was concluded that the LDG could not have cooled from the melt in seconds, nor did it cool from high temperatures over geological periods of time. This suggested that the samples of LDG were not ejecta, that they were not quenched in rapid flight from either a volcanic event or a meteor impact.

VI RAMAN SPECTROSCOPY OF INSULATING THIN FILMS

Galeener, Stutius and McKinley [C2] developed a special sample manipulator, enabling them to launch a guided wave in a thin film, image the path of the (wave-guided) laser beam onto the entrance slit of a Raman spectrometer, and obtain polarized Raman spectra from the thin film guide. The long path length thus sampled enabled acquisition of high signal to noise spectra (S/N ~ 1000/1) and should facilitate the study of thin film growth-induced defects by Raman scattering. The first Raman spectra of amorphous sputtered Nb_2O_5, Ta_2O_5 and CVD-deposited Si_3N_4 were thus obtained and reported [C2]. Preliminary analysis suggested that the Nb and Ta are orthogonally six-coordinated to O atoms, while the N lies at the center of an equilateral triangle of (tetrahedrally-coordinated) Si atoms. This interpretation is supported by the more sophisticated machinery that has been developed in this research program. It now appears that we have developed sufficient theoretical tools to enable exploitation of this experimental method in our forthcoming studies [10] of process induced defects in insulating thin films.

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9. J. Robertson, Central Electricity Research Laboratories, Leatherhead, U.K. (private communication).
10. A proposal entitled "Defects in Amorphous Insulators" is in preparation, to be submitted to the ONR.

C. PUBLICATIONS UNDER CONTRACT N00014-80-C-0713

C1 "Network Dynamics"
M.F. Thorpe and F.L. Galeener
Phys. Rev. B 22, 3078 (1980).

C2 "Electron Microscopy and Raman Spectroscopy of Nb_2O_5, Ta_2O_5 and Si_3N_4 Thin Films"
F.L. Galeener, W. Stutius and G.T. McKinley
in the Physics of MOS Insulators, eds. G. Lucovsky, S.T. Pantelides and F.L. Galeener, (Pergamon, New York, 1980), p. 77.

C3 "Raman and Inelastic Neutron Scattering by Vitreous $ZnCl_2$"
F.L. Galeener, J.C. Mikkelsen, Jr., A.C. Wright, R.N. Sinclair, J.A.E. Desa and J. Wong
J. Non-Cryst. Solids 42, 23 (1980).

C4 "Correlated Excitations and Raman Scattering in Glasses"
R.M. Martin and F.L. Galeener
Phys. Rev. B 23, 3071 (1981).

C5 "Raman Diffusion Profilometry: OH in Vitreous SiO_2"
F.L. Galeener and J.C. Mikkelsen, Jr.
Appl. Phys. Lett. 38, 336 (1981).

C6 "Vibrational Dynamics in ^{18}O-Substituted Vitreous SiO_2"
F.L. Galeener and J.C. Mikkelsen, Jr.
Phys. Rev. B 23, 5527 (1981).

C7 "Vibrational Selection Rules in Disordered Solids: Vitreous GeO_2"
F.L. Galeener
J. Phys. (Paris) 42(C6), 24 (1981).

C8 "Planar Rings in Vitreous Silica"
F.L. Galeener
J. Non-Cryst. Solids 49, 53 (1982).

C9 "Phonons in Glasses"
F.L. Galeener
in Excitations in Disordered Systems, ed. M.F. Thorpe, (Plenum, New York, 1982), p. 359
(NATO Summer Institute Lecture Series).

C10 "Raman Studies of Glass Structure"
F.L. Galeener
in Raman Spectroscopy, Linear and Nonlinear, eds. J. Lascombe and P.V. Huong, (Wiley Hayden, Chichester, 1982), p. 529.

C11 "Planar Rings in Glasses"
F.L. Galeener
Solid State Commun. 44, 1037 (1982).

C12 "Vibrational Probes of Glass Structure"
F.L. Galeener
Kinam, 4(C), 83 (1982)
CIFMO (Mexican Government) Workshop.

C13 "Raman Studies of B_2O_3 Glass Structure: ^{10}B-^{11}B Isotopic Substitution"
F.L. Galeener and A.E. Geissberger
J. Phys. (Paris) 44(C9), 343 (1983).

C14 "Vibrational Evidence for Intermediate Range Order in Glasses"
F.L. Galeener
in the Structure of Non-Crystalline Materials II, eds. P.H. Gaskell, A.E. Davis and J.N. Parker, (Taylor and Francis, London, 1983), p. 337.

C15 "Raman Studies of Vitreous B_2S_3 and Polycrystalline $(HBS_2)_3$"
A.E. Geissberger and F.L. Galeener
in The Structure of Non-Crystalline Materials II, eds. P.H. Gaskell, A.E. Davis and J.N. Parker, (Taylor and Francis, [illegible]don, 1983), p. 381.

C16 "A Comparison of the Neutron, Raman and Infrared [illegible]brational Spectra of Vitreous SiO_2, GeO_2 and BeF_2"
F.L. Galeener, A.J. Leadbetter and M.W. Stringf[illegible]w
Phys. Rev. B 27, 1052 (1983).

C17 "Vibrational Dynamics in ^{30}Si-Substituted Vitreous SiO_2"
F.L. Galeener and A.E. Geissberger
Phys. Rev. B 27 6199 (1983).

C18 "Raman Studies of Vitreous SiO_2 Versus Fictive Temperature"
A.E. Geissberger and F.L. Galeener
Phys. Rev. B 28, 3266 (1983).

C19 "Vibrational Dynamics in Isotopically Substituted Vitreous GeO_2"
F.L. Galeener, A.E. Geissberger, G.W. Ogar, Jr., and R.E. Loehman
Phys. Rev. B 28, 4768 (1983).

C20 "Rings in Central Force Network Dynamics"
F.L. Galeener and M.F. Thorpe
Phys. Rev. B 28, 5802 (1983).

C21 "On the Thermal History of Libyan Desert Glass"
F.L. Galeener, A.E. Geissberger and R.A. Weeks
J. Non-Crystalline Solids (in press).

C22 "The Vibrational Bethe Lattice with Random Dihedral Angles"
R.A. Barrio, F.L. Galeener and E. Martinez
Phys. Rev. Letters (in press).

D. INVITED TALKS (BY F.L. GALEENER) UNDER ONR CONTRACT N00014-80-C-0713

T1 "Network and Defect Vibrations in Glasses"
Annual Meeting of the American Ceramic Society
Washington, D.C., May, 1981.

T2 "Applications of Raman Spectroscopy to the Elucidation of Glass Structure"
Sixth University Conference on Glass Science
Pennsylvania State University
University Park, PA, July, 1981.

T3 "Phonons in Glasses"
NATO Adv. Study Institute on Excitations in Disordered Solids
Michigan State University
E. Lansing, MI, August, 1981.

T4 "Vibrational Probes of Glass Structure"
Amorphous Silicon Workshop
Centro Internacional de Fisica y Matematicas Orientados
Cuernavaca, Morelos, Mexico, January, 1982.

T5 "Raman Selection Rules in Halide Glasses"
First Int'l. Symposium on Halide and Other Non-Oxide Glasses
Cambridge University
Cambridge, England, March, 1982.

T6 "Vibrational Evidence for Intermediate Range Order in Glass Structure"
Int'l. Conference on the Structure of Non-Crystalline Materials II
Cambridge University
Cambridge, England, July 1982.

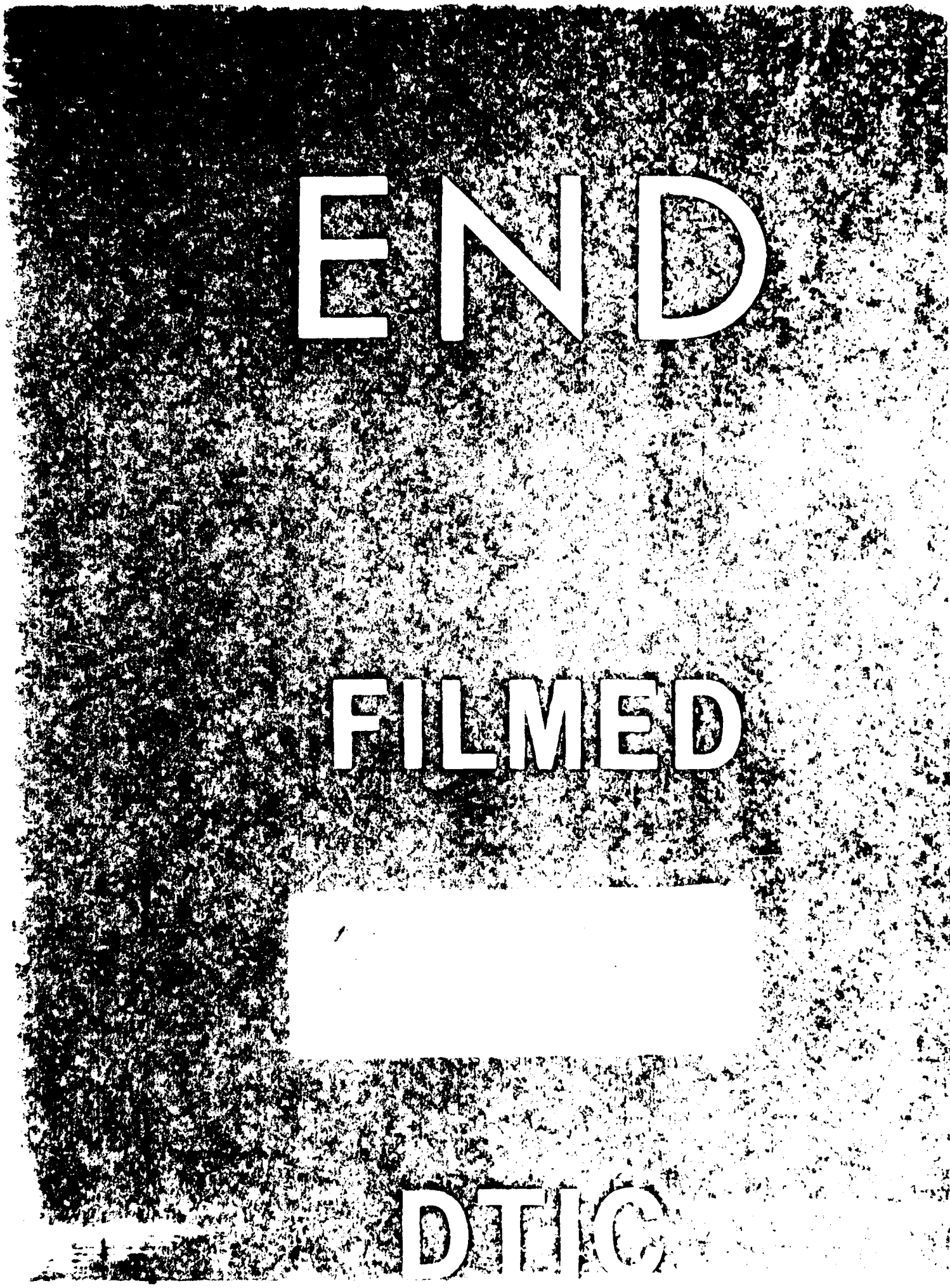
T7 "Raman Studies of Glass Structure"
Eighth Int'l. Conference on Raman Spectroscopy
Universite de Bordeaux
Bordeaux, France, September, 1982.

T8 "Regular Rings in Glasses"
American Physical Society March Meeting
Los Angeles, March, 1983.

T9 "Raman Studies of Regular Rings in Glasses"
Int'l. Symposium on Structure and Bonding in Non-Crystalline Solids
Reston, VA, May, 1983.

T10 "On the Thermal History of Libyan Desert Glass"
Int'l. Conference on Glass in Planetary and Geological Phenomena
Alfred, NY, August, 1983.

T11 "Raman Studies of the Thermal History of Insulating Glasses"
Int'l Conference on the Modes of Formation of Glass
Vanderbitt University
Nashville, TN, July, 1984.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