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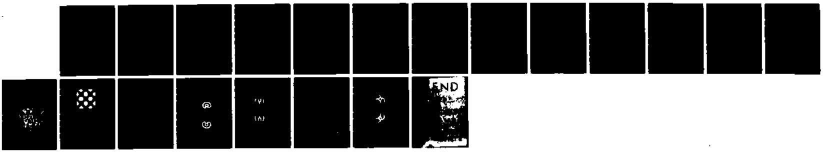

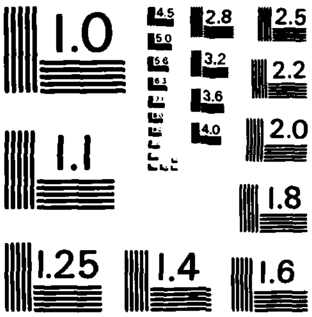

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Electronic Structure, Chemical Bonding, and Superconductivity of Silver Films on Germanium	5. TYPE OF REPORT & PERIOD COVERED Interim
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K. H. Johnson	8. CONTRACT OR GRANT NUMBER(s) N00014-81-K-0499
9. PERFORMING ORGANIZATION NAME AND ADDRESS Center for Materials Science and Engineering, M.I.T., Cambridge, Massachusetts 02139	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. Nr 056-757
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217	12. REPORT DATE September 10, 1984
	13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approval for public release; distribution unlimited.	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	
18. SUPPLEMENTARY NOTES Prepared for Publication in Solid State Communications	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) electronic structure chemical bonding superconductivity silver films on germanium	Pi

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NOV 1984

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

The local electronic density of states and chemical bonding of a very thin Ag film on a Ge substrate have been calculated by the partitioned scattered-wave molecular-orbital method. The partial occupation of "layered" Ag $p\pi$-bonding molecular orbitals at the Fermi energy, resulting from covalent bonding with the Ge substrate, is responsible for the incipient superconductivity recently observed by Burns et al. for very thin epitaxially grown Ag films on Ge. These orbitals are unoccupied in nonsuperconducting pure Ag.

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OFFICE OF NAVAL RESEARCH
Contract No. N00014-81-K-0499
Task No. Nr 056-757

TECHNICAL REPORT NO. 9

ELECTRONIC STRUCTURE, CHEMICAL BONDING, AND SUPERCONDUCTIVITY OF SILVER FILMS ON GERMANIUM

by

K. H. Johnson

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

September 10, 1984

ELECTRONIC STRUCTURE, CHEMICAL BONDING, AND SUPERCONDUCTIVITY OF SILVER FILMS ON GERMANIUM*

K. H. Johnson
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Abstract

The local electronic density of states and chemical bonding of a Ag monolayer film on a Ge (001) substrate have been calculated by the partitioned scattered-wave molecular-orbital method. The partial occupation of spatially delocalized "layered" Ag pπ-bonding molecular orbitals at the Fermi energy, resulting from weak covalent bonding with the Ge (001) substrate, is responsible for the incipient superconductivity recently observed by Burns _et al._ for very thin epitaxially grown Ag films on Ge (001). In pure Ag, which is not a superconductor, the pπ-bonding molecular orbitals are unoccupied. The occupation of spatially localized Ag s,p σ^*-antibonding molecular orbitals around the Fermi energy is responsible for the observed two-dimensional metallic localization effects on the electrical conductivity above the superconducting transition temperature.

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*Research sponsored by the Office of Naval Research.

In a recent publication [1], Burns et al. have reported the onset of an incomplete superconducting transition in very thin epitaxially grown Ag films on a Ge (001) substrate at temperatures below 2°K. In another recent paper [2], a molecular-orbital basis for understanding the incidence of superconductivity in materials has been described. In the present communication, it is shown that the latter theoretical approach can be used to explain the incipient superconductivity of thin Ag films on Ge.

Consider first a metal, such as aluminum, which is normally superconducting in bulk, thin-film, and small-particle forms at temperatures less than 2°K. In Ref. 2 it was shown that the electronic structure of Al aggregates at the Fermi energy is characterized by spatially delocalized "layered" $p\pi$-bonding molecular orbitals of the type displayed in the two- and three-dimensional contour maps of Figs. 1 and 2, respectively. This molecular-orbital topology, in conjunction with the dynamic Jahn-Teller effect (the "virtual phonons" of BCS theory [3]), was shown in Ref. 2 to lead to the "antferromagnetic" spin polarization of conduction electron pairs (the "Cooper pairs" of BCS theory) at the Fermi energy over the layered orbitals of Fig. 2, producing the superconducting state at the transition temperature

$$k_B T_c \sim [h^2/4\pi (mM)^{1/2} d^2] \exp(-h^2/2me^2 d) \qquad (1)$$

In the above expression, d is the distance between the centroids of the layered molecular-orbital components (see Fig. 2), M is the atomic mass, m is the electron mass, e is the electron charge, h is Planck's constant, and k_B is the Boltzmann constant. In Ref. 2, expression (1) has been shown to be equivalent to the conventional BCS formula for T_c and leads to values of the transition temperature in good agreement with experiment.

Consider now the example of pure silver, which is normally not a superconductor. One can compute the local electronic structure of this material in bulk, particle, or thin-film form with the recently developed iterative partitioned scattered-wave molecular-orbital method [4]. In this approach, the extended solid-state system is spatially partitioned into subclusters for which the local electronic densities of states and molecular orbitals are computed iteratively, <u>including</u> the effects of "embedding" the subclusters in the surrounding extended environment. For a pure Ag monolayer having the cubic structure shown in Fig. 3(a), the resulting local density of states at T = $0^{\circ}K$ for the encircled Ag_4 subcluster, including the effects of coupling this subcluster to the surrounding monolayer atoms, is shown in Fig. 4. The high-density manifold of states between 4 and 6 eV below the Fermi energy E_F is associated with the Ag 4d orbitals and corresponds to the fully occupied d-band of bulk crystalline silver. The Fermi energy itself coincides with a smaller peak in the density of states, corresponding to spatially localized s,p σ^*-<u>antibonding</u> molecular orbitals of the type mapped in Fig. 5. Approximately 1 eV above the Fermi energy is a peak in the density of states that corresponds to pπ-bonding molecular orbitals of the type mapped in Fig. 6. The latter orbitals are the monolayer analogues of the spatially delocalized layered $p\pi$-bonding orbitals shown above (see Figs. 1 and 2) and in Ref. 2 to be responsible for the superconducting state of aluminum. Since these states are unoccupied in pure silver, they cannot lead to superconductivity in this metal unless they are somehow brought into coincidence with the Fermi energy. This explains why pure silver is not superconducting under normal conditions.

How then is one to understand the observation of Burns et al. [1] that very thin Ag films epitaxially grown on a Ge (001) substrate are virtually superconducting? The local electronic density of states at $T = 0^{\circ}K$ for a Ag monolayer (Fig. 3(a)) supported on a Ge (001) substrate (Fig. 3(b)), computed by the same procedure used above for the unsupported Ag monolayer, is plotted in Fig. 7. The Fermi energy now coincides with a peak in the density of states corresponding to molecular orbitals that are $p\pi$-bonding within the Ag monolayer and $p\sigma$-bonding with respect to the Ge substrate. A contour map for one of these orbitals is plotted in Fig. 8. The Ag s,p σ^*-antibonding orbitals (Fig. 5) which coincide with the Fermi energy in pure Ag (Fig. 4) correspond to the peak in Fig. 7 for Ge-supported Ag located $\sim$1 eV above the Fermi energy. In other words, there is an effective reversal of the Ag s,p σ^*-antibonding and Ag $p\pi$ -bonding molecular orbitals around the Fermi energy in going from a pure unsupported Ag monolayer to a Ag monolayer supported on Ge, due to covalent bonding between the monolayer and the substrate. It should be emphasized, however, that this bonding is relatively weak because it involves the overlap of otherwise unoccupied virtual delocalized $p\pi$ molecular orbitals of the Ag film with localized $p\sigma$ orbitals of the coordinatively unsaturated surface atoms of the Ge substrate (see Fig. 8). There is no net bonding between the other atomic orbitals of Ag and Ge, because the contributions of the Ag(s,d)-Ge(p) σ-bonding molecular orbitals are cancelled out by the fully occupied σ^*-antibonding ones (see Fig. 7). The "layered" topology of the composite Ag(p)-Ag(p)π/Ag(pπ)-Ge(p)σ molecular orbitals at the Ag-Ge interface is reasonably close to that shown above to be a precursor of the superconducting state. Substitution of the computed Ag $p\pi$ layer orbital distance d = 2.8 A into expression (1) leads to a transition temperature $T_c \sim 2.2^{\circ}K$, in good agreement with the observations of Burns et al.. The fact that the latter investigators were not able to observe a complete superconducting transition in the Ge-supported Ag films can possibly be explained by the "imperfect" character of the layered $p\pi$ molecular-orbital topology at the Ag-Ge interface, evident in Fig. 8, as compared to the more ideal $p\pi$ orbital topologies shown in Figs. 1 and 6.

Finally, Burns et al. [1] have reported that, above the superconducting transition temperature, the electrical conductivity of very thin Ag films on Ge (001) is dominated by the metal film and displays properties characteristic of metallic weak localization in two dimensions. This observation can also be addressed on the basis of the present theoretical model. At higher temperatures, the s,$p\sigma^*$-antibonding electronic states of the Ag film, i. e. those responsible for the peak in the density of states of the Ag-Ge system immediately above the $T = 0^{\circ}K$

Fermi energy E_F (see Fig. 7), become accessible to the conduction electrons which, at temperatures near absolute zero, are confined to the layered $p\pi$-bonding orbitals. Within the Ag film, these antibonding orbitals have the spatially localized character shown in Fig. 5. In other words, the "scattering" of conduction electrons into localized metal-metal antibonding states in the Ag film at higher temperatures could be responsible for the observed two-dimensional localization characteristics of the conductivity.

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Figure Captions

Fig.1. Contour map of the $p\pi$-bonding molecular-orbital wavefunction at the Fermi energy of a 43-atom face-centered-cubic aluminum cluster, plotted in the (200) crystallographic plane up to second-nearest neighbors. The solid and dashed contours represent positive and negative values, respectively, of the wavefunction.

Fig.2. Three dimensional contour map (the 3-d version of Fig. 1) showing the "layered" topology of the $p\pi$-bonding molecular-orbital wavefunction at the Fermi energy of a 43-atom aluminum cluster. This layered topology is believed to be a precursor to superconductivity in aluminum (see Ref. 2).

Fig.3. (a) Spatial partitioning of a Ag monolayer film into a Ag_4 subcluster (encircled) and its surrounding environment; (b) Structure of a Ge substrate looking along the (001) direction.

Fig.4. Subcluster local electronic density of states for a pure Ag monolayer film, as computed by the partitioned scattered-wave method. The principal bonding, nonbonding, and antibonding characters of the component molecular orbitals are indicated.

Fig.5. Contour map of the $s,p\sigma^*$-antibonding molecular-orbital wavefunction corresponding to the density-of-states peak at the Fermi energy (Fig. 4) of a pure Ag monolayer film, plotted in the vicinity of two nearest-neighbor Ag atoms. The solid and dashed contours represent positive and negative values, respectively, of the wavefunction.

Fig.6. Contour map of the $p\pi$-bonding molecular-orbital wavefunction corresponding to the density-of-states peak immediately above the Fermi energy (Fig. 4) of a pure Ag monolayer film, plotted in the vicinity of two nearest neighbor Ag atoms. The solid and dashed contours represent positive and negative values, respectively, of the wavefunction.

Fig. 7. Subcluster local electronic density of states for a Ag monolayer film supported on a Ge (001) substrate, as computed by the partitioned scattered-wave method. The principal bonding, nonbonding, and antibonding characters of the component molecular orbitals are indicated.

Fig. 8. Contour map of the composite Ag-Ag $p\pi$-bonding/Ag-Ge $p\sigma$-bonding molecular-orbital wavefunction corresponding to the density-of-states peak at the Fermi energy (Fig. 7) of a Ag monolayer film supported on a Ge (001) substrate. The contours are plotted in a plane perpendicular to the Ge (001) surface through two nearest-neighbor Ag nuclei.

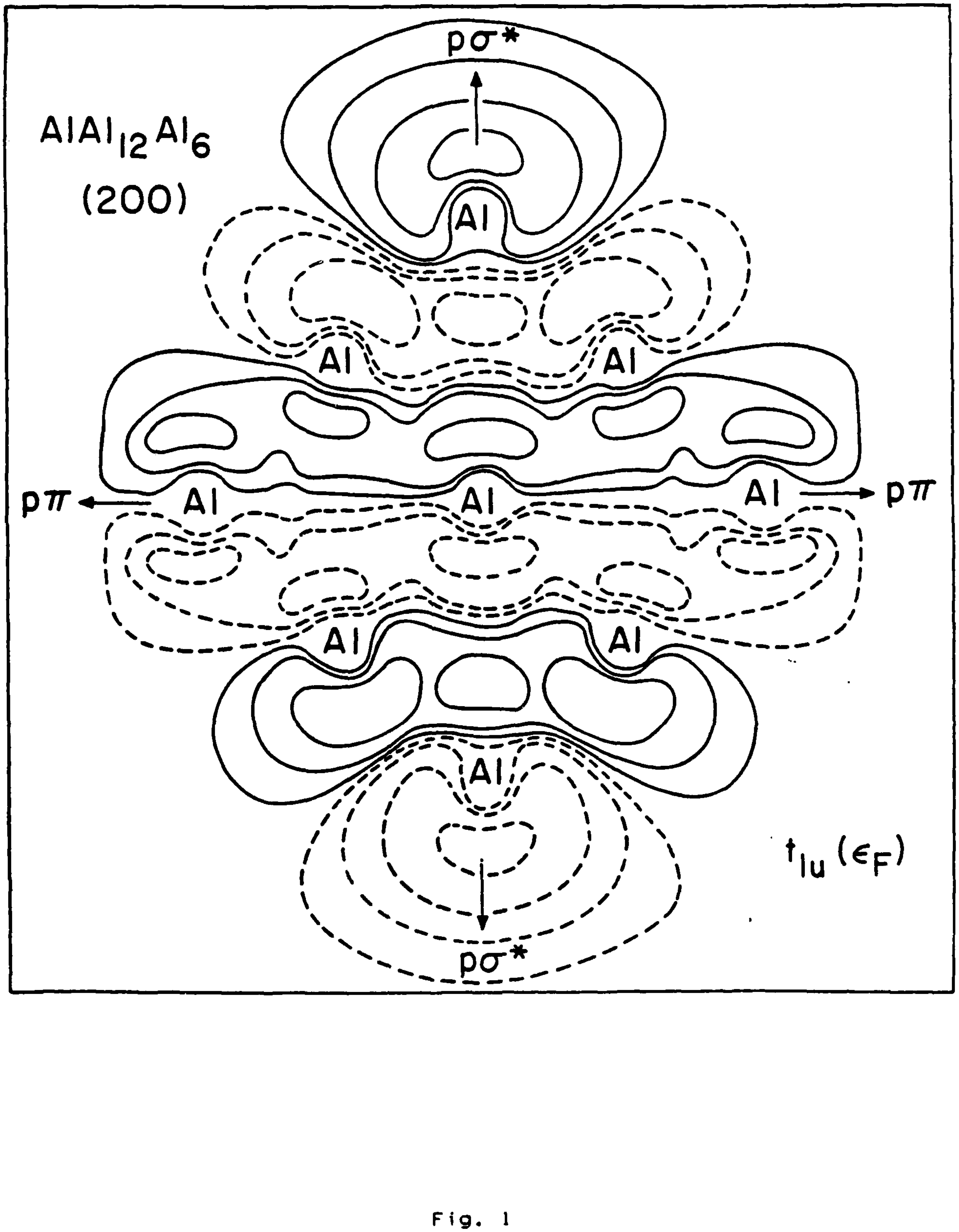

Fig. 1

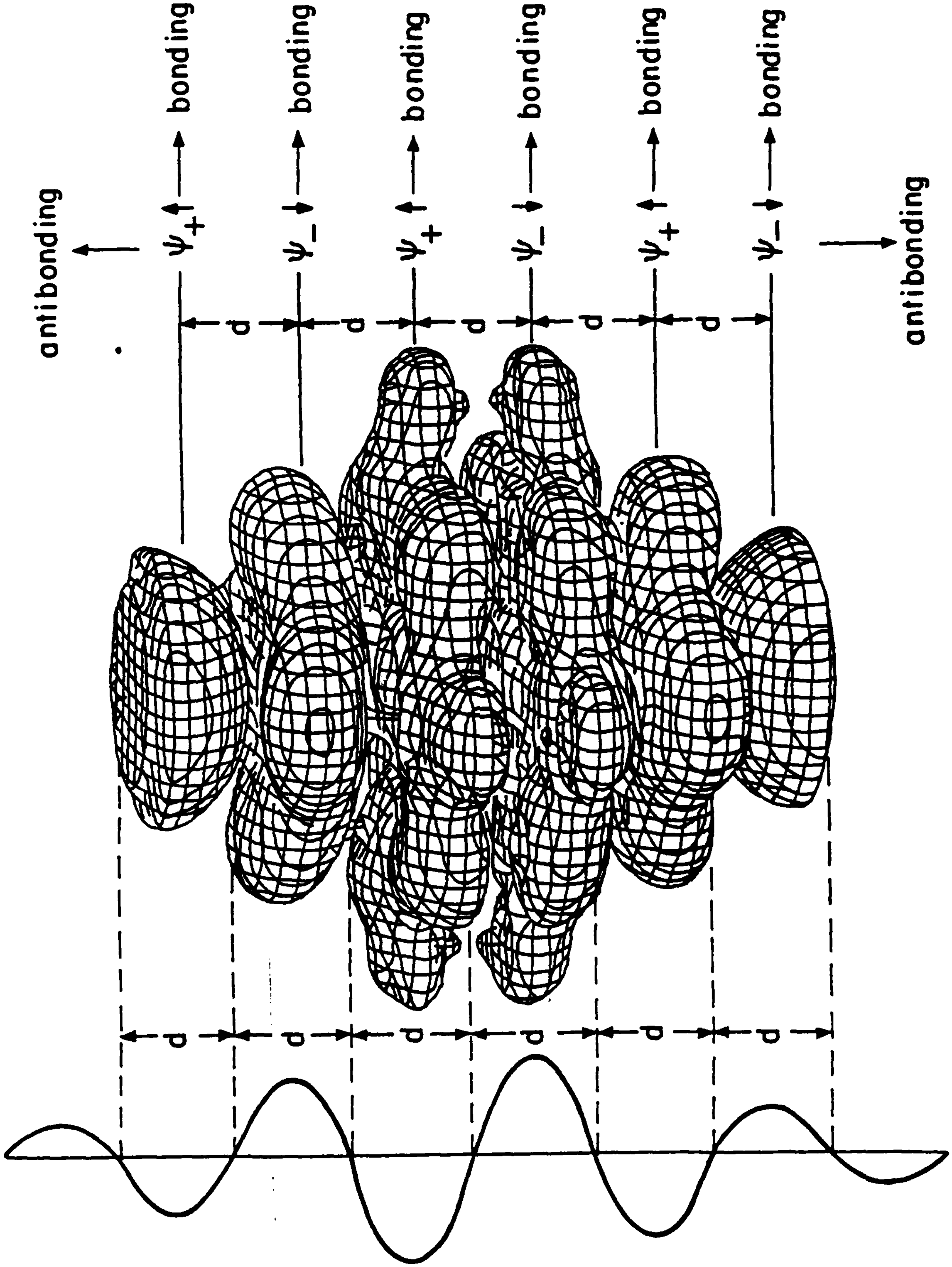
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Fig. 2

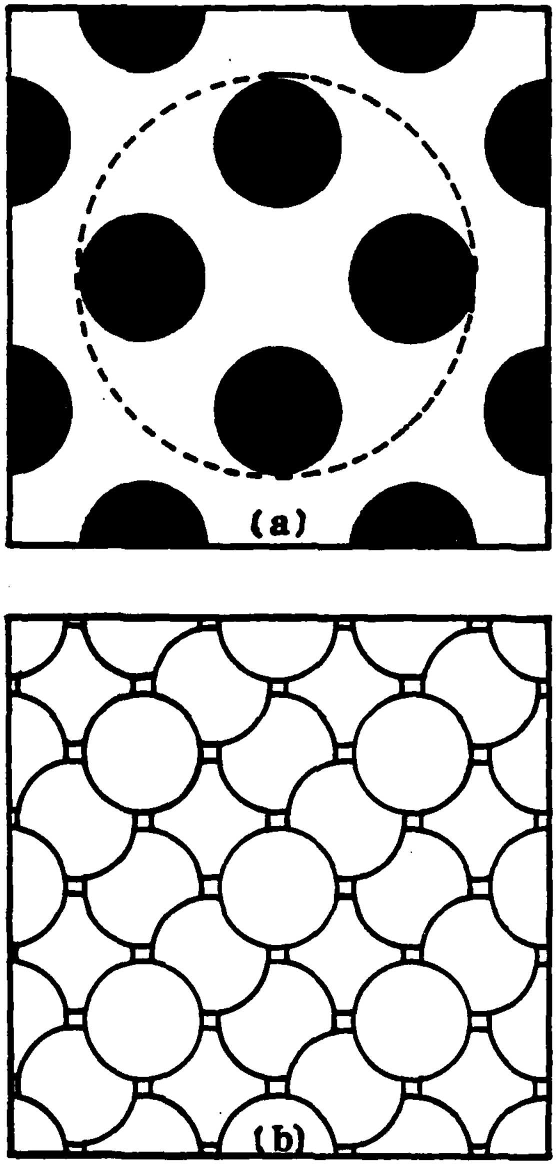
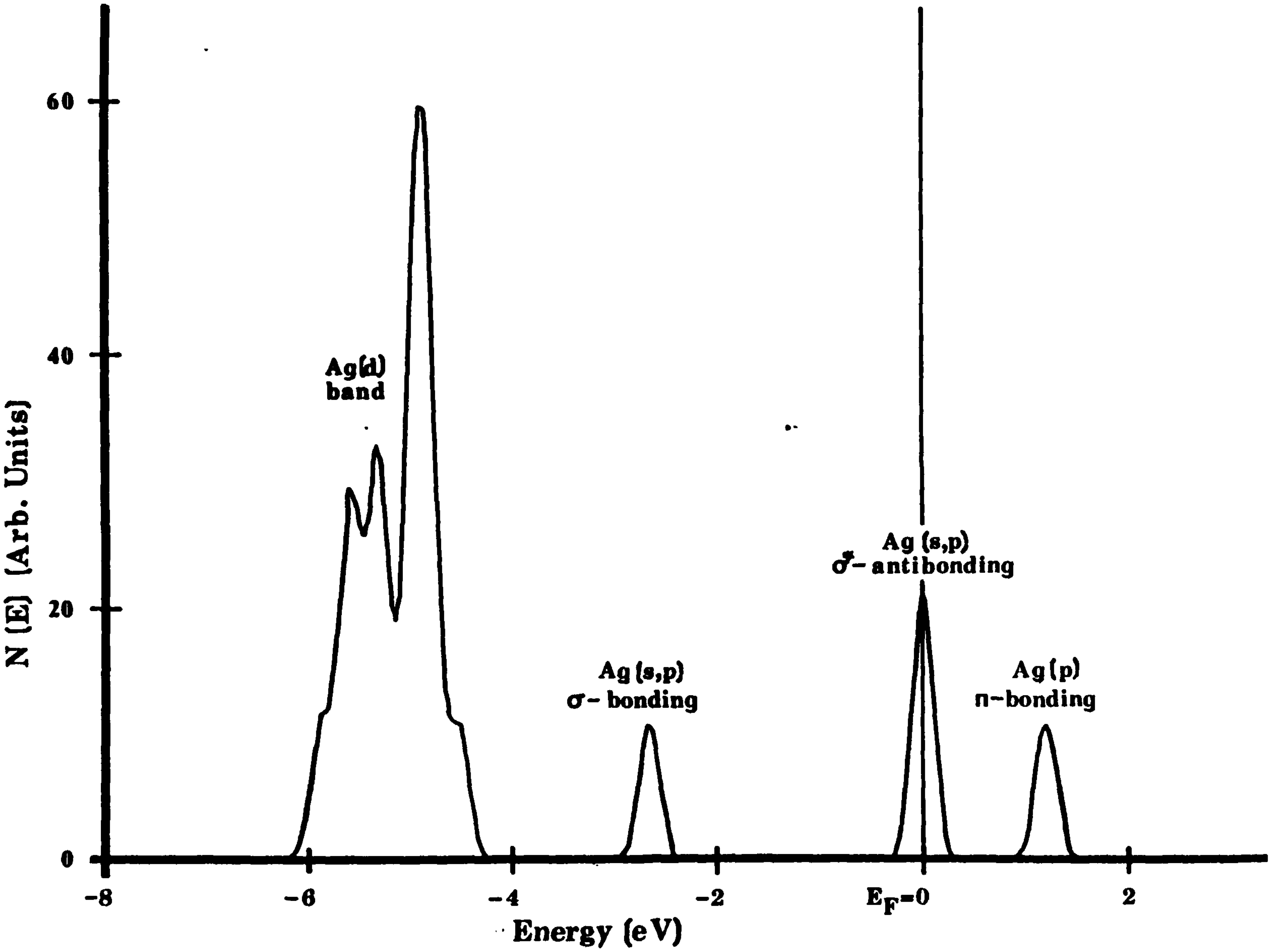


Fig. 3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Ag (s,p) σ- bonding
Ag (s,p) σ^*- antibonding
Ag (p) π-bonding

Fig. 4

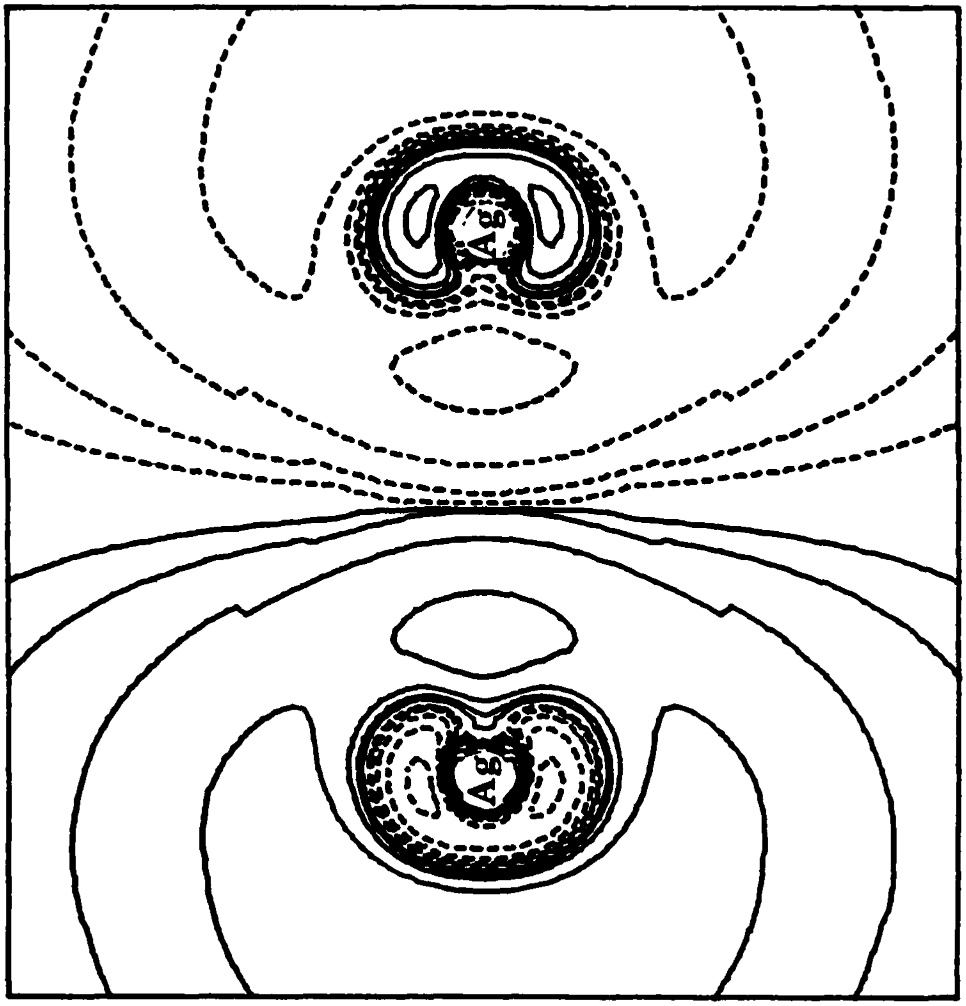


Fig. 5

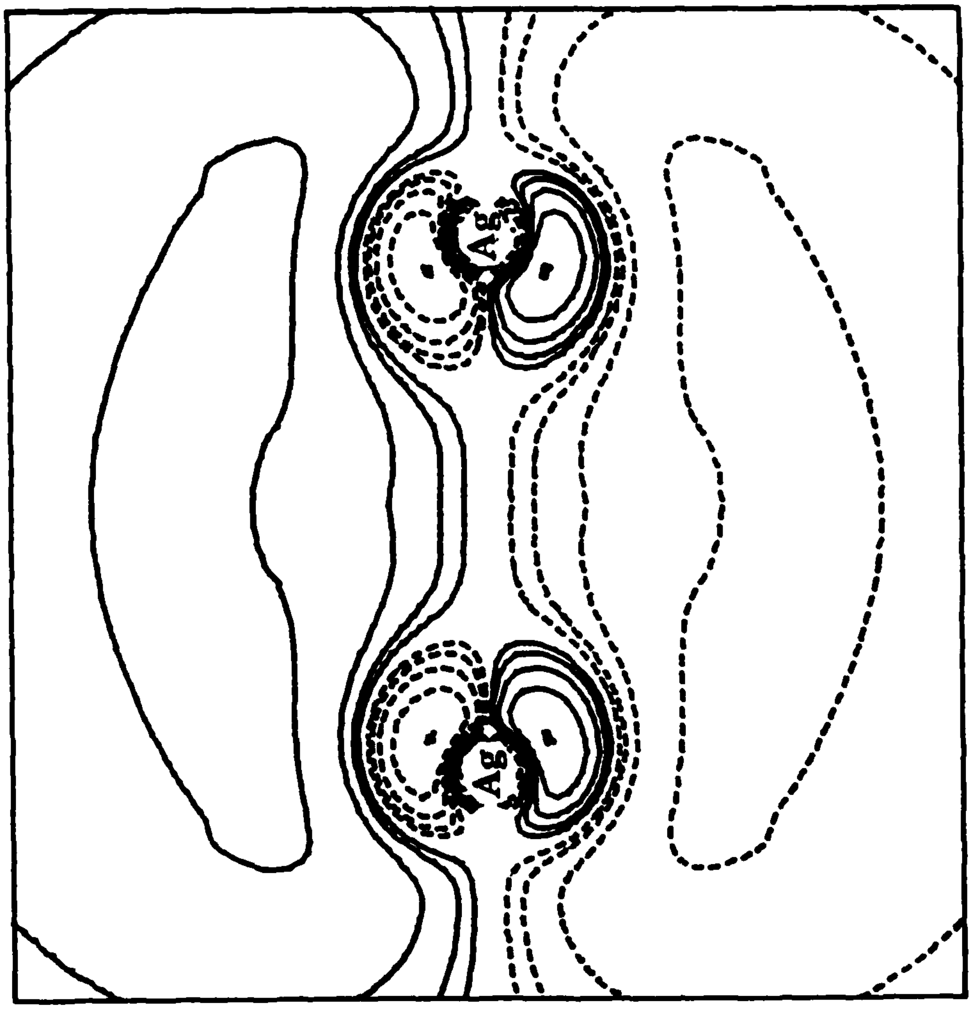
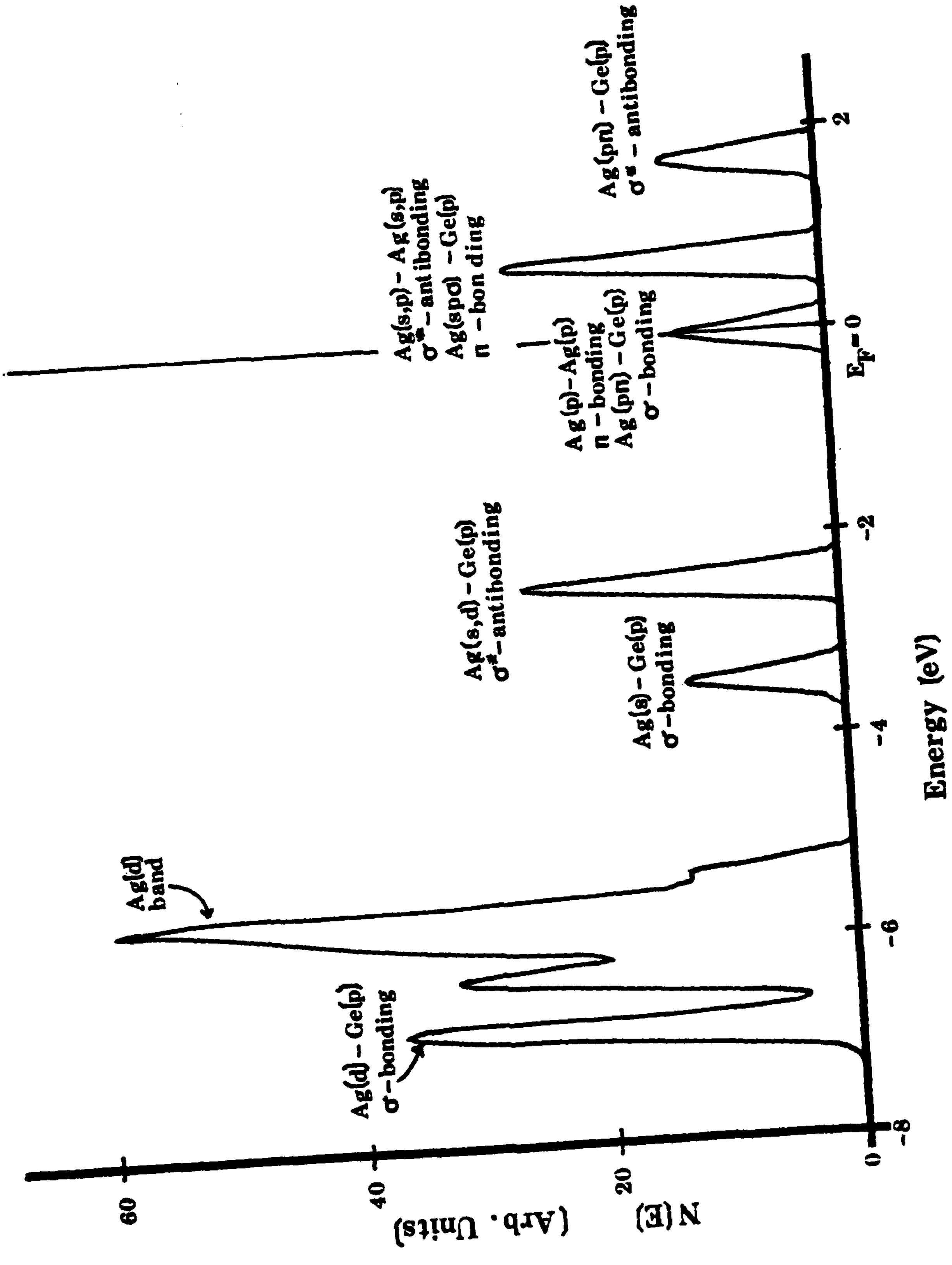


Fig. 6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2
Ag(d) band
Ag(d) - Ge(p)
σ-bonding
Ag(s,d) - Ge(p)
σ*-antibonding
Ag(s) - Ge(p)
σ-bonding
Ag(s,p) - Ag(s,p)
σ*-antibonding
Ag(spσ) - Ge(p)
π-bonding
Ag(p)-Ag(p)
π-bonding
Ag(pπ) - Ge(p)
σ-bonding
Ag(pπ) - Ge(p)
σ* - antibonding

Fig. 7

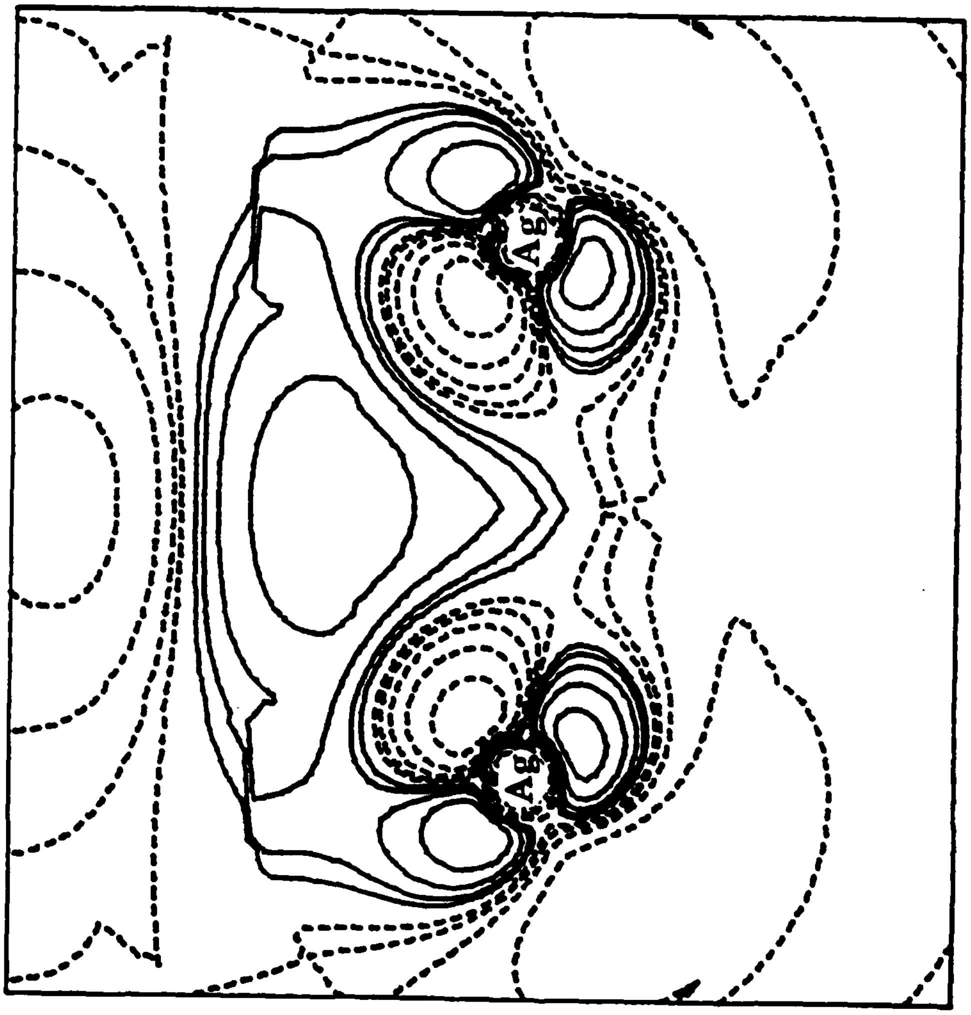

Fig. 8

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