# Experimental energy bands of a rare-earth metal: Gd(0001)

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We have determined energy bands of Gd metal at room temperature with the use of angle-resolved photoelectron spectroscopy with synchrotron radiation. Along the central sixfold axis of the Brillouin zone, we find the two critical points of the $6s,5d_{z^2}$-type band ($\Gamma_4^-$ at $E_F-1.4$ eV and $\Gamma_1^+$ at $E_F-2.8$ eV) and a critical point of a final-state band ($\Gamma_4^-$ at $E_F+6.6$ eV) in qualitative agreement with band calculations. At the zone boundary $5d$ states are observed along the $ML$ line at about $E_F-0.35$ eV corresponding to an $L_1$ point. Unoccupied $4f$ states appear in the secondary-electron emission within 1.6 eV of the vacuum level. The work function of Gd(0001) is $3.3\pm0.1$ eV.

## INTRODUCTION

The rare-earth (RE) metals and their compounds have a peculiar electronic structure, since the $5d,6s$ valence states are often energetically degenerate with the shallow core-like $4f$ states. This leads to interesting phenomena such as a mixed valence in many RE compounds and highly complex magnetic structures in the RE metals.[1] Gadolinium is a prototype RE metal due to its half-filled $4f$ shell, which makes Gd a particularly stable trivalent metal with three conduction electrons ($5d,6s^2$). In addition, only Gd exhibits simple ferromagnetism ($T_C=293$ K, $\mu=7.6\mu_{\rm Bohr}$) among the RE elements. For RE systems, the occupation number for core electrons and the density of states for band electrons have been studied using photoelectron spectroscopy[2,3] and isochromat spectroscopy.[3] For Gd, optical measurements have been performed[4] and de Haas–van Alphen data[5] exist to determine its Fermi surface. However, no band dispersions or critical points have been measured for any of the RE's, although several band-structure calculations exist (for Gd, see Refs 6–9). In analogy with other elemental RE's there exist occupied $5d$ states in Gd (about one $5d$ electron per atom). The $4f$ shell of Gd is half-filled with all seven spins aligned parallel according to Hund's rule. These spins form a localized magnetic moment which makes Gd the only simple elemental ferromagnet[1] apart from the transition metals Fe, Co, and Ni. The latter exhibit itinerant (i.e., bandlike) ferromagnetism[10] caused by the $3d$ electrons, whereas in Gd the localized $4f$ moment dominates with seven Bohr magnetons over the $5d,6s$ electrons which carry 0.6 Bohr magneton according to neutron scattering data[11] and band calculations.[7] The occupied $4f$ levels (i.e., the peak position of the $4f^6$ multiplet after photoionization) is found at $7.9\pm0.1$ eV below $E_F$ and the empty $4f$ levels (i.e., the peak position of the $4f^8$ multiplet after adding a $4f$ electron in isochromat spectroscopy) is at $4.3\pm0.1$ eV above $E_F$.[3] The $5d$ states are believed to be bandlike and a ferromagnetic exchange splitting of $\sim0.5$ eV has been calculated near $E_F$.[7]

We have used angle-resolved photoemission with synchrotron radiation on a Gd(0001) surface to determine energy and momentum of the $5d$ states. At the Brillouin-zone center, we find the critical points $\Gamma_4^-$ at $E_F-1.4$ eV and $\Gamma_1^+$ at $E_F-2.8$ eV in fair agreement with the non-self-consistent band calculations of Dimmock and Freeman.[6] As predicted by theory,[6,7] $d$ states near $E_F$ are found only at the boundary of the Brillouin zone. The large gap of states above the $\Gamma_4^-$ point at the zone center affects[12] the interpretation of the spin-polarized photoemission data.[13] Our findings represent the first experimental band-structure determination for a RE metal. They demonstrate that the concepts of angle-resolved photoemission originally developed for transition and noble metals[14] also work out in the presence of a partially filled $f$ shell.[15]

## EXPERIMENTAL

The key to obtaining band dispersions from angle-resolved photoemission data is the preparation of an atomically clean well-ordered surface. Because of the high chemical reactivity of the RE metals, few attempts have been made to prepare such surfaces (see Ref. 16 for Lu and Sc which have a similar $s^2d$ valence-electron configuration as Gd). We have used a basal plane from a single crystal grown by B. J. Beaudry at Ames National Laboratories, which was electropolished in 90% methanol and 10% perchloric acid at dry-ice temperature with a current density of $\sim10$ mA/cm$^2$. This leaves a well-ordered surface passivated by a chloride layer. The chloride was removed by sputter-annealing cycles with annealing temperatures up to $\sim600$ °C during sputtering (annealing temperatures above $\sim700$ °C produced a rough surface by subliming Gd). Small remaining amounts of surface carbon could be removed by reaction with adsorbed oxygen at the expense of residual surface oxygen. The results presented below were obtained from surfaces which had C(273 eV)-to-Gd(138 eV) Auger peak ratios between 0.02 and 0.06 and O(513 eV)-to-Gd(138 eV) peak ratios between 0.01 and 0.03 and a small residual Fe contamination. Gd(0001) exhibited a sharp $(1\times1)$ low-energy electron diffraction (LEED) pattern and photoemission results independent of the actual C-to-O Auger peak ratio. Care had to be taken to obtain a well-ordered surface. In particular, excessive sputtering or heating above $\sim700$ °C produced a disor-

dered surface without angular dependence of the photoemission peaks, with very weak emission from the bands below $E_F - 1$ eV and without a visible LEED pattern. A sensitive test of surface order was provided by the intensity and width of the surface $4f$ core-level emission.[17] The photoemission experiments were performed with a display spectrometer[18] at the Synchrotron Radiation Center of the University of Wisconsin.

## RESULTS

With the use of angle-resolved photoemission with a tunable synchrotron radiation light source, we have determined critical points of the Gd valence bands. Band-mapping methods are described in more detail elsewhere.[14] Here we use mainly the fact that critical points are characterized by an extremal behavior of transition intensities and of binding energies. This is exemplified in Fig. 1 where photoelectron spectra are shown for emission normal to the basal Gd(0001) plane. The momentum parallel to the surface $\vec{k}^{\parallel}$ is zero because of momentum conservation, i.e., a line in momentum space (see Fig. 2) is scanned. The momentum perpendicular to the surface ($\vec{k}^{\perp}$) is tuned by varying the photon energy and reaches diffferent points of a final-state band [see arrow in Fig. 3(a)]. Although the detailed structure of the final-state bands is unknown, one can assume that over a wide enough photon energy range, all $k^{\perp}$ values are reached. The initial-state energies of the principal transition in Fig. 1 range between $-2.8$ and $-1.4$ eV. We assign these two energies to the critical points $\Gamma_1^+$ and $\Gamma_4^-$ of the only occupied band in qualitative agreement with the calculations of Refs. 6–8 [see Fig. 3(a)]. The symmetry character of these two critical points is $s,d_{z^2}$. The symmetry assignment in Fig. 3(a) (from Ref. 6) is analogous to the $d$ bands in hcp transition metals[19] and agrees with the labels in Refs. 7 and 8 except for the lowest $\Gamma$ point. The $\Gamma_1^-$ symmetry assigned to this point in Refs. 7 and 8 would have $g$ character.[20] The local maximum in initial-state energy around $h\nu = 8.0$ eV (Fig. 1) indicates a $\Gamma$ point in the final-state bands around 6.6 eV above $E_F$. Similar to hcp transition metals, an $s,p$-like critical point with $\Gamma_4^-$ symmetry exists in this energy range which is associated with a free-electron-like band [see dashed curve in Fig. 3(a)]. The symmetry and topology of this band may be changed by the unoccupied $4f$ states in Gd which are very close in energy (see Fig. 3 shaded area and Ref. 3).

In transition metals it is possible to obtain not only critical-point energies, but also energy-band dispersions between critical points by measuring the continuous movement of interband transitions with photon energy.[14] A dispersing peak can be observed in Gd between 7.5 and 10 eV photon energy (Fig. 1). At higher photon energies, however, only a switch in intensity between the two critical points is seen. This is due to a strong $k^{\perp}$ broadening which is related to the exceptionally short mean-free path $l_e$ of photoelectrons in the RE metals. Values of about two interplanar spacings have been obtained[17] for $l_e$ from the ratio of surface-to-bulk core-level emission on polycrystalline films, and our data on single-crystal Gd(0001) indicate an even shorter mean free path between 20 and 40 eV kinetic energy. With $l_e$ comparable to the interplanar spacing the uncertainty in $k^{\perp}$ becomes comparable to the size of the unit cell in $k$ space, i.e., the Brillouin zone. Therefore, a certain averaging over $k^{\perp}$ is going on and critical points with high density of states become enhanced. The $k^{\perp}$ broadening becomes less severe close to

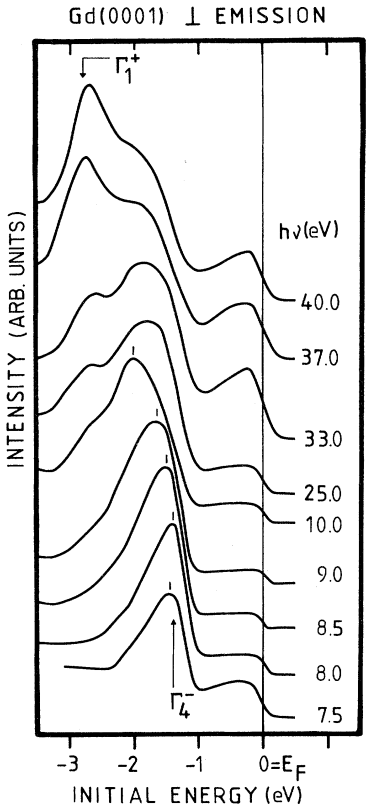


FIG. 1. Normal-emission photoelectron spectra from Gd(0001) for different photon energies $h\nu$. The extremal peak positions are assigned to the critical points $\Gamma_1^+$ and $\Gamma_4^-$ of the lowest valence band.

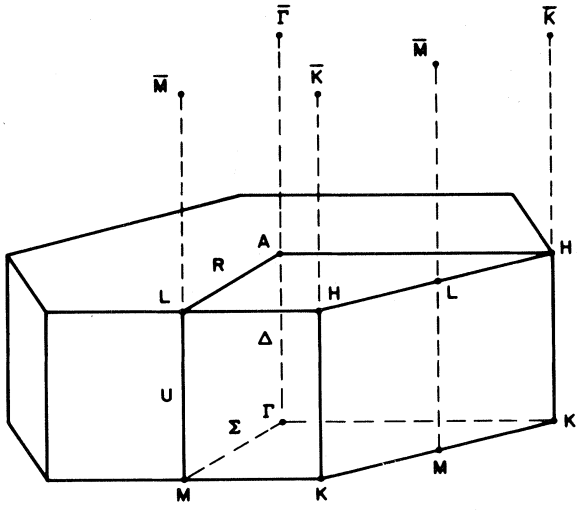


FIG. 2. Bulk and surface Brillouin zones for Gd(0001).

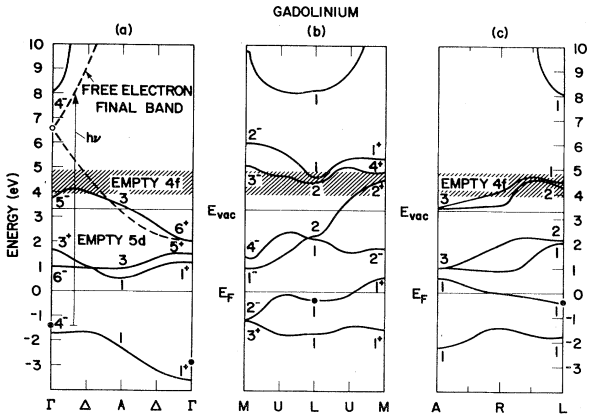


FIG. 3. Comparison of calculated energy bands (full lines from Ref. 6) with experimental critical-point energies (dots) for Gd. The bands are unfolded according to Ref. 19 similar to the $d$ bands of hcp transition metals.

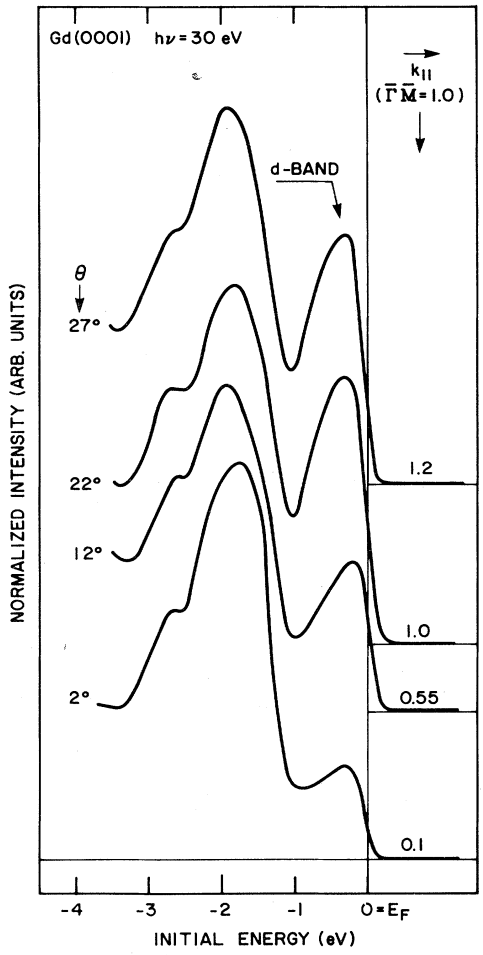


FIG. 4. Angular-dependent photoelectron spectra from Gd(0001) at $h\nu=30$ eV. $5d$-like states appear below $E_F$ near the zone boundary.

the photothreshold. The width of the direct-transition peaks (tickmarks in Fig. 1) decreases for photon energies below 10 eV and the second feature at $-2.7$ eV (due to the $\Gamma_1^+$ critical point) disappears. This apparent increase in the mean free path below 10 eV photon energy is consistent with the threshold for the principal energy-loss feature (peak at 12 eV with about 5 eV full width[21]) which has been assigned to a bulk plasmon.

Photoelectron spectra for off-normal emission are shown in Fig. 4. At the particular azimuth chosen for Fig. 4 one scans from the center $\bar{\Gamma}$ of the surface Brillouin zone at $k^{||}=0$ (equivalent to the line $\Gamma A\Gamma$ in the bulk) to the $\bar{M}$ point at the zone boundary at $k^{||}=1.0$ Å$^{-1}$ (equivalent to the line $MLM$ in the bulk) and back to $\bar{\Gamma}$ a $k^{||}=2.0$ Å$^{-1}$ (see Fig. 2). The salient feature in off-normal emission (see Fig. 4) is a band near the Fermi level $E_F$ which crosses $E_F$ at about $0.5\bar{\Gamma}\bar{M}$ and moves down to $E_F-0.35$ eV at $\bar{M}$. A similar structure is seen along other azimuths (not shown). The intensity near $E_F$ is strongest around the $\bar{M}$ point (at $h\nu=33$ eV). This is visualized in the two-dimensional display of the photoelectron emission from states near $E_F$ (Fig. 5) where not only $\bar{M}$ points of the first Brillouin zone but also of the second zone are seen. These observations can be explained qualitatively by band calculations[6–8] (see Fig. 3) which give occupied $d$ bands near $E_F$ at the zone boundary (e.g., around $L_1$ at $E_F-0.3$ eV) but not at the zone center. These bands cross the Fermi level about halfway between the zone center and the boundary [e.g., along $A_1L_1$ in Fig. 3(c)]. The critical points at the zone boundary cannot be determined as accurately as the zone center since $k^{\perp}$ is very much lifetime broadened (see above) for the final-state energies of about $E_F+30$ eV used in Figs. 4 and 5. Similar to the normal

TABLE I. Comparison of experimental and calculated critical points of energy bands for gadolinium. Energies are in eV relative to $E_F$. $\Phi$ is the work function.

| | This experiment (near $T_c$) | Calculation (Ref. 6) (paramagnetic) | Calculation (Refs. 7 and 8) (ferromagnetic) Spin up | Spin down |
|---|---|---|---|---|
| $\Gamma_1^+$ | $-2.8^{+0.1}_{-0.3}$ | $-3.5$ | $-3.2$ | $-3.1$ |
| $\Gamma_4^-$ | $-1.4^{+0.15}_{-0.05}$ | $-1.7$ | $-1.6$ | $-1.3$ |
| $L_1$ | $-0.35\pm0.15$ | $-0.3$ | | |
| $\Gamma_4^-$ | $+6.6\pm0.5$ | $+8.1$ | | |
| $\Phi$ | $3.3\pm0.1$ | | | |

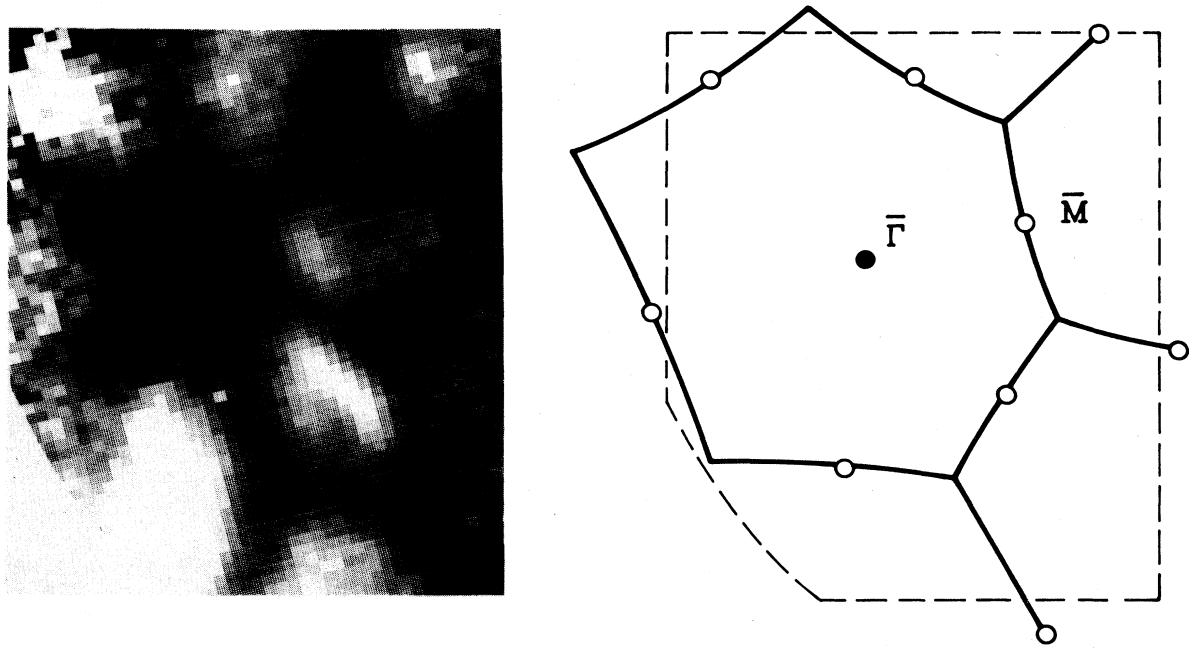


FIG. 5. Picture of the emission pattern for electrons excited from the Fermi level with 33 eV photon energy. The strongest emission is seen around the $\bar{M}$ points (see Fig. 2).

emission data we expect mainly the critical points with high density of states to show up. For the $\bar{M}=MLM$ line the calculated critical points cluster around two values ($L_1=-0.3$ eV, $L_1,M_1^+,M_3^+,M_2^-$ between $-1.1$ and $-1.7$ eV) in agreement with the two main experimental peaks ($-0.35$ and $-1.8$ eV). The zone boundary at $\bar{M}$ becomes inaccessible from the Gd(0001) surface for final-state energies below $E_F+7.1$ eV since the necessary escape angle approaches 90° from the normal. This escape cone effect will also affect spin-polarized photoemission[12,13] because the spin-polarized $d$ states are located near $E_F$ around the zone boundary $MLKH$ and not at $\Gamma$. A summary of our experimentally determined critical points and a comparison with theory is given in Table I.

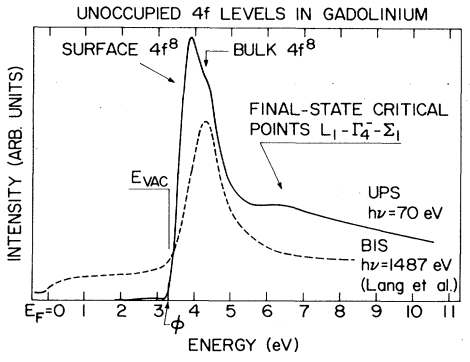


FIG. 6. Angle-integrated spectrum of secondary electrons (excited at $h\nu=70$ eV) showing conduction-band features and the unoccupied $4f$ levels. For comparison, an isochromat spectrum of the unoccupied $4f$ states in the bulk (from Ref. 3) is shown.

The spectrum of secondary electrons in Fig. 6 gives information about unoccupied states. The structure at $E_F+6.5$ eV is assigned to the high density of states at the bottom of an $s,p$-like band ($\Gamma_4^-,L_1,\Sigma_1$) in agreement with our determination of the $\Gamma_4^-$ point at $E_F+6.6$ eV from direct transitions. The large peak near the vacuum level is related to unoccupied $4f$ states. We can exclude analyzer transmission effects causing such a structure, since we carefully compensated the contact potential and compared the spectra with other metals which give rounded edges without an extra peak. From the width of the energy distribution curve we determined the work function of Gd(0001) to be $3.3\pm0.1$eV.

The increase in intensity below the bulk $4f$ level (given by the x-ray isochromat spectrum[3]) may be due to an unoccupied surface core level but other possibilities cannot be ruled out (e.g., an accumulation of electrons at the bottom of the bulk $4f$ states). It would be interesting to determine the position of the unoccupied $4f$ level at the surface. Two different mechanisms for surface core-level shifts could be distinguished, namely, the purely initial-state shift (due to a different electrostatic potential at the core) and the purely final-state shift (due to a different screening at the surface relative to the bulk). The initial-state effect shifts occupied and empty states in the same direction. The final-state effect shifts them in opposite directions. For the occupied $4f$ states of polycrystalline Gd a shift of $-0.48$ eV (i.e., towards higher binding energy at the surface) has been reported.[17] Our data on single-crystal Gd(0001) indicate a somewhat larger shift in the same direction.

For the future, angle-resolved photoemission at higher photon energies ($h\nu\gtrsim100$ eV) will lead out of the low escape depth regime with large $k$ broadening and will allow

an actual mapping of the bands between the critical points. It will also be interesting to measure at low temperature to determine the ferromagnetic exchange splitting of the $d$ bands. Low temperature would also reduce the phonon-assisted transitions which partially destroy the momentum information at room temperature and at high photon energies. For a better test of the band picture, self-consistent band calculations are desirable.

*Note added in proof.* Recently, self-consistent relativistic, and spin-polarized band calculations have been performed by P. Strange, H. H. Wills, and W. M. Temmermann (unpublished). Compared with the results of Refs. 6–8 the majority-spin $f$ levels are shifted by about 1.1 eV, and the $d$ bands are shifted by about 0.3 eV. This shift in energy makes the agreement with our experimental critical points less favorable. Furthermore, the ferromagnetic exchange splitting is much larger in this calculation (1.5 eV at $\Gamma_1^+$ and 1.3 eV at $\Gamma_4^-$) than in Refs. 7 and 8 (0.1 and 0.3 eV, respectively).

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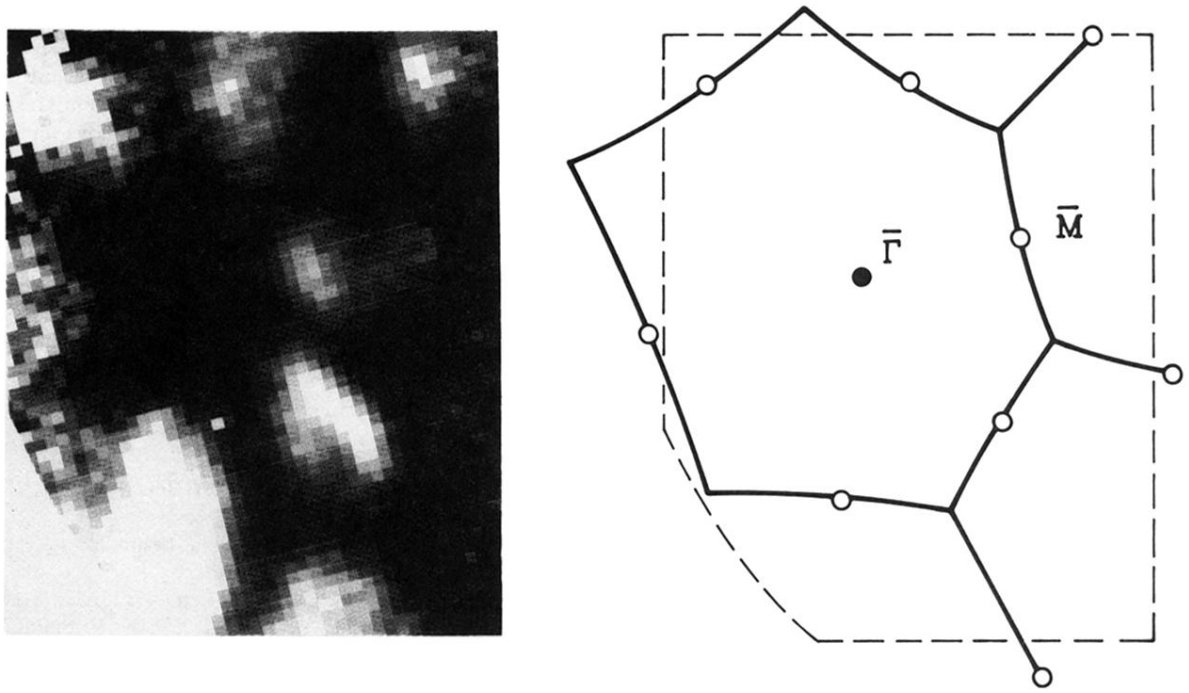


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