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MECHANISMS FOR CLEAVAGE AND INTERGRANULAR EMBRITTLEMENT IN FE

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ABSTRACT

The mechanism of cleavage in bcc Fe has been investigated with electronic structure calculations and compared to similar calculations modeling cleavage in other bcc materials (Li, Nb, Mo). It has been found in the BCC materials we have studied that those known to undergo (100) cleavage show enhancement of the density of states (DOS) on the virtual surface layer as the material is strained to failure. Using total energy calculations it is shown that there is a point of inflection (corresponding to the point of maximum force versus displacement) in the total energy at nearly the same point as the maximum enhancement in the DOS. We conjecture that this point represents the transition state for the fracture process. Extending these ideas, the electronic structure near a Fe(111) grain boundary has been calculated both with and without segregated P. We find clear evidence for the formation of a P band of states, suggesting the existence of P-P interactions within the segregated layer. A chemical model of strain-induced bond failure is suggested in which bonds parallel to the fracture surface compete with the cohesive Fe-Fe bonds normal to the surface.

INTRODUCTION

Our approach to the study of mechanical behavior of metallic materials, and to the study of fracture in particular, has been to use first principles quantum mechanical calculations to study the electronic structure of a host of materials which exhibit a variety of mechanical responses. Then correlations between the known mechanical properties and features observed in the calculated electronic properties are used to provide a microscopic understanding. This is an extension of the method by which the structure property relationships of metallurgy were established and represents an extension from the uncovery of relationships between crystal structure and properties.

Until recently, a first principles study of fracture has been complicated by an inability to model the fracture process. Therefore, the correlations which have been established are between features of the intrinsic mechanical behavior and the electronic structure of the starting (unfractured) material (1). By far the more interesting and technologically rewarding area of investigation is the electronic evolution

associated with the fracture process. It is, after all, the competition between the evolution of a crack and the emission of a dislocation which represents the deformation process. Therefore an initial understanding of the changes in the electronic structure accompanying cracking is an area which must be studied before a complete electronic understanding of deformation can be obtained.

In this paper we use the layer Korringa-Kohn-Rostoker (LKKR) electronic structure technique (2,3,4) to study the evolution of the (100) cleavage process in bcc Fe and the properties of an ideal Fe(111) grain boundary and the electronic influence of segregated P impurities at this boundary. The LKKR approach provides an accurate and elegant solution to the Schrödinger equation, within the self-consistent field and local spin density approximations, for an infinite solid and only assumes translational symmetry in two directions. The method models an isolated defect by embedding a slab containing the defect in two semi-infinite bulk regions and since Fe is magnetic, allows spin-polarization of both bulk and interface regions. The mathematical details and physical approximations involved in LKKR interface calculations are discussed in detail in refs. (2,3,4), and rather than reproduce the details here, we refer the reader to these papers. The technique is thus ideally suited for studying interfaces in bulk materials such as the (111) grain boundary as well as the cleavage process.

RESULTS

- *(100) cleavage of Fe*

The initial studies of cleavage on the (100) planes of Fe were undertaken by modelling a simple interface in which only two interplanar spacings were expanded from the bulk. This geometry is shown schematically in Fig. 1.

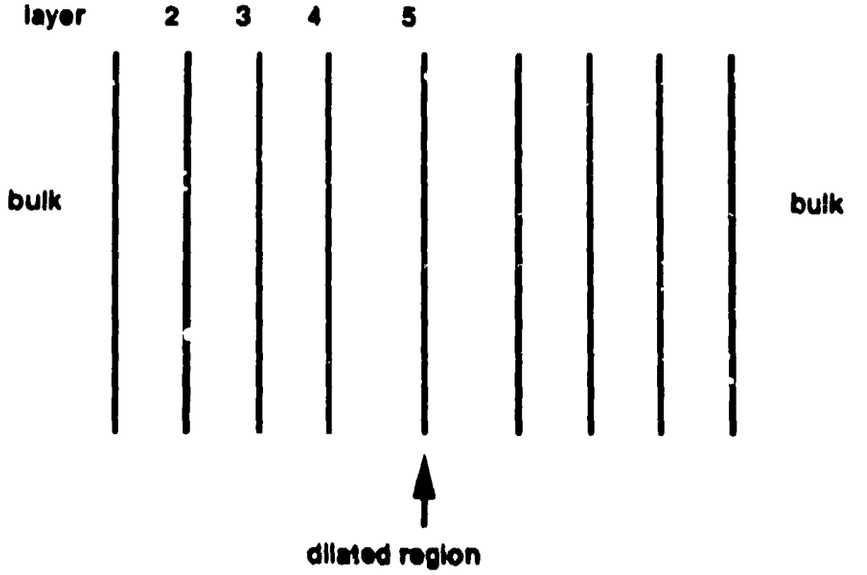
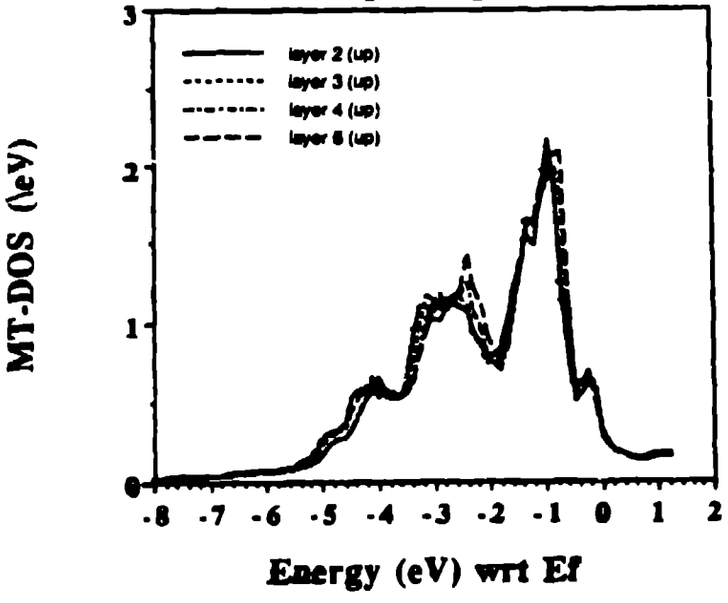


Figure 1: Interface chosen to model (100) cleavage

Fig. 2a: Fe cleavage 10% expansion

spin up



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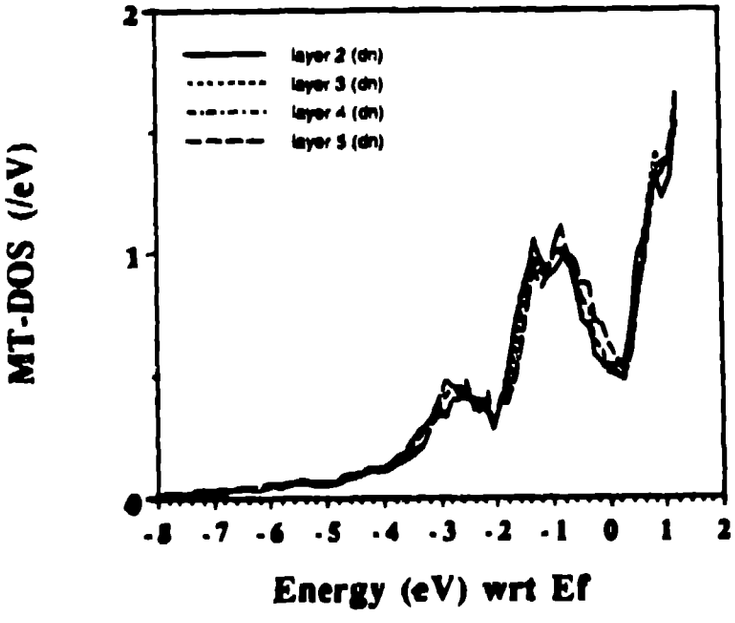

Fig. 2b: Fe cleavage 30% expansion

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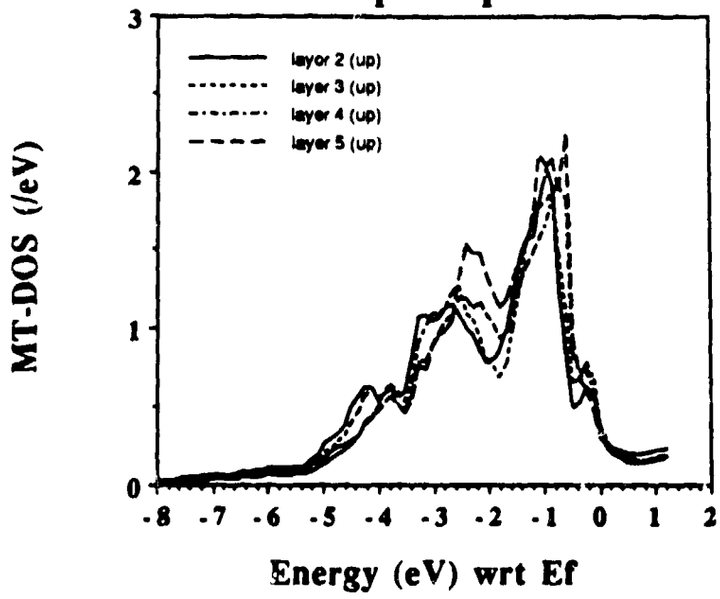

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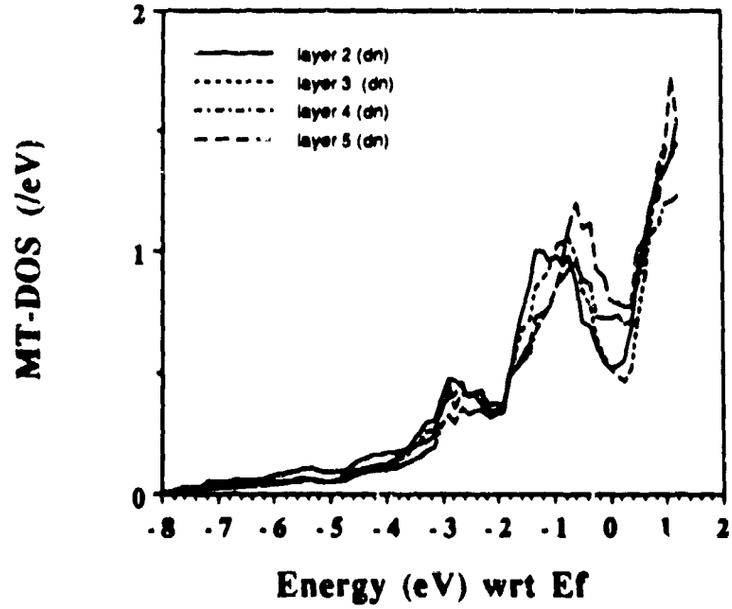

Fig. 2c: Fe cleavage 42% expansion

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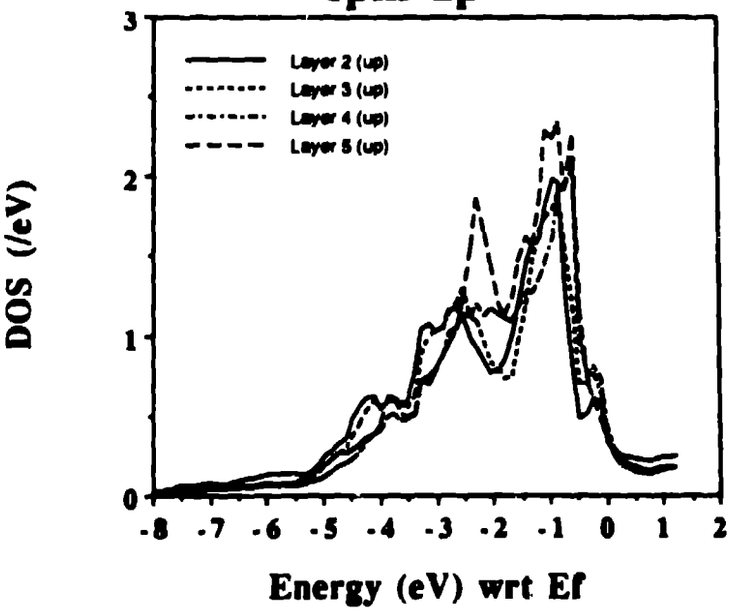

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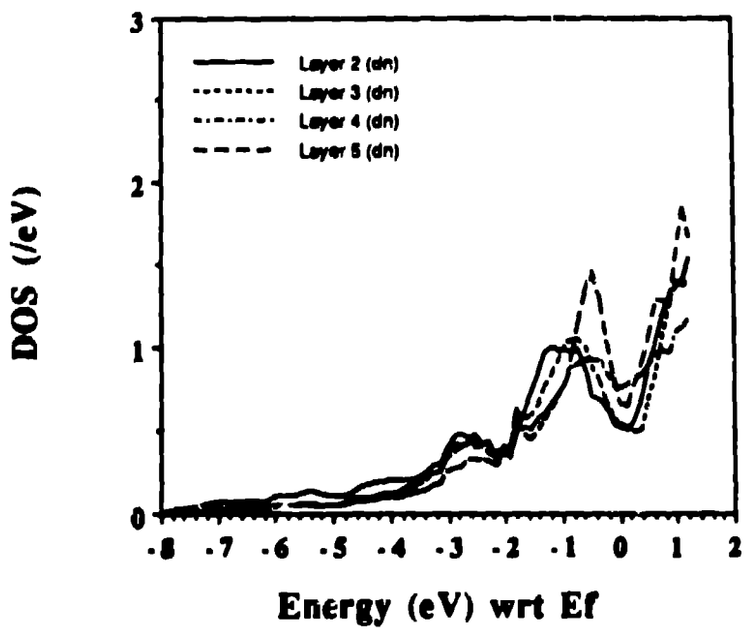

Fig. 2d: Fe cleavage 50% expansion

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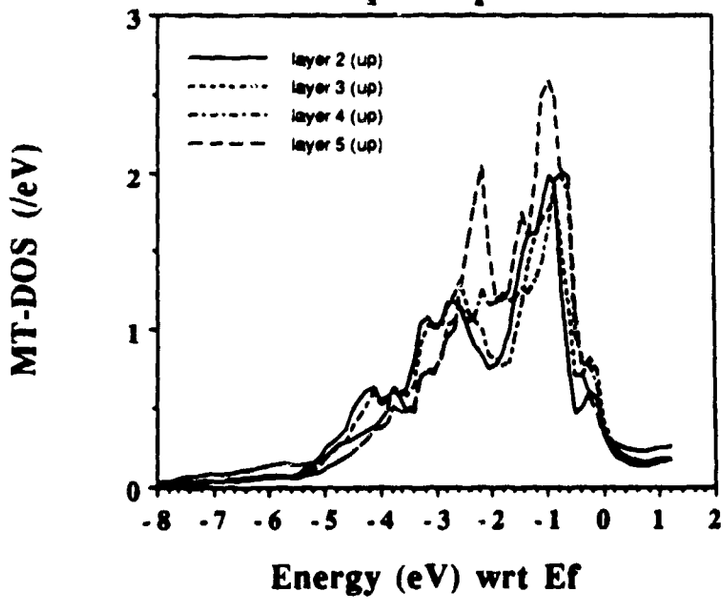

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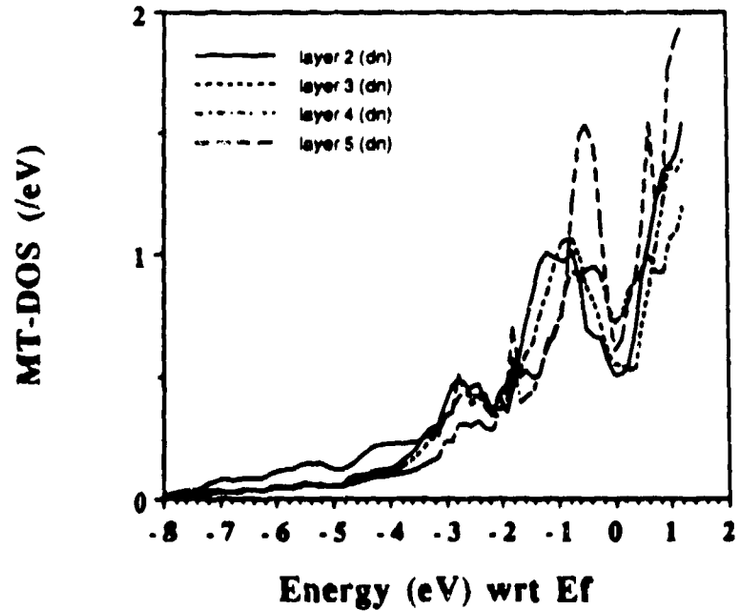


Four calculations have been performed corresponding to expansions between layers 4 and 5 of 10%, 30%, 42% and 50% over the bulk interplanar spacing. The DOS for each of the layers as a function of separation for both majority and minority spins is shown in Fig. 2. Beginning with the initial dilation of 10% (Fig 2a) the DOS near the Fermi energy on the center layer (layer 5) is enhanced relative to the bulk, this is particularly apparent on the spin down band. This enhancement is maximum somewhere between 30% and 42%. (Figs. 2b and 2c) The 42% expanded layer spacing (Fig. 2d) produces a central three layer region where the structure is rigorously fcc. We have postulated in a previous work (5), using ideas suggested by Bader *et al.* (6) for identifying bonds from structures in the total charge density, that by symmetry fcc crystals only have first neighbor bonds though bcc crystal have both first and second neighbor bonds. Thus the 42% expansion corresponds to the breaking of the second neighbor (100) bonds, present in all bcc materials, at the interfacial layer and should correspond to the maximum in the force versus displacement curve. To confirm this, the total energy for the four layer separations has been computed and is shown graphically in Figs. 3. We expect the maximum in the force versus displacement curve to correspond to a point of inflection in the total energy versus separation curve of Fig. 3. As is clearly seen such an inflection point exists between the 30% and 42% dilations. Further confirmations is provided in Fig. 4, where the electronic pressure, which corresponds to an average pressure, is plotted. A maximum in the electronic pressure is seen at approximately the same expansion as the inflection point in the total energy.

We take all of this information as a strong indication that the maximum in the force versus displacement curve occurs near an interlayer spacing where the coordination is locally fcc and thus the second neighbor bonds that exist, by symmetry within the bcc structure are being broken. At this interlayer spacing, we postulate, that the second neighbor bonds parallel to the virtual fracture surface are competing with the second neighbor bonds across the fracture surface. At greater interlayer spacing the formation of bounds parallel to the surface are energetically more favorable than those across the interface and serve to lower surface energy. Hence the point of maximum strain during (100) cleavage is the point where bonds normal to the fracture surface are exactly compensated by bonds parallel to the fracture surface. This conjecture is consistent with the enhancement of the DOS near the Fermi energy (E_F) on the forming surface layer. An enhancement of the DOS near E_F is a feature we associate with the changes in bonding from perpendicular to parallel to the interface resulting from the lifting of degeneracy along (100) directions by the strain. In an alternative picture, the DOS near E_F is a measure of the susceptibility of a system to respond to some external perturbation. In our case the external perturbation is a stress and the response is a strain. The enhancement of the DOS near E_F on the central layer suggests that the atomistic mechanism for cleavage is strain localization to the atomic bonds across cleavage plain. In the limit of infinite separation, two free surfaces are formed in which atomic relaxations at these surfaces will be small compared to that between the surfaces. Thus the strain can be thought of as fully localized between these two surfaces.

Fig 3: Total Energy vs Separation

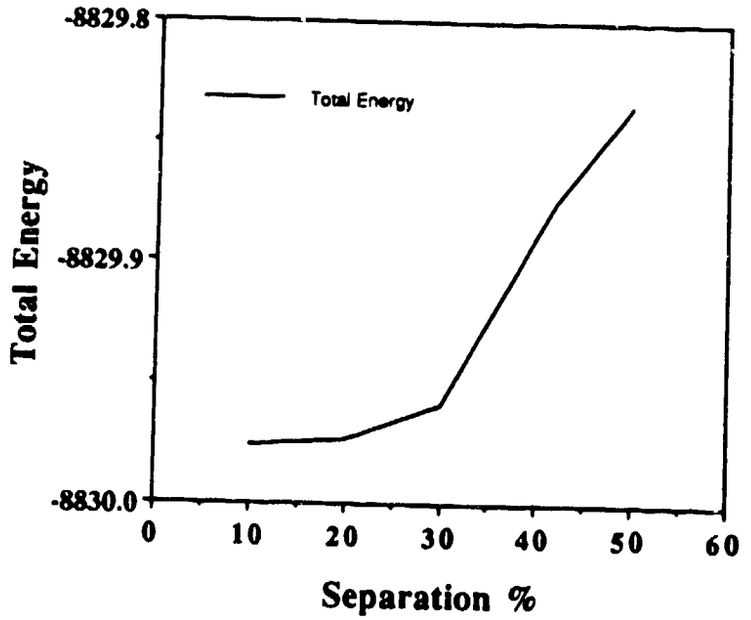
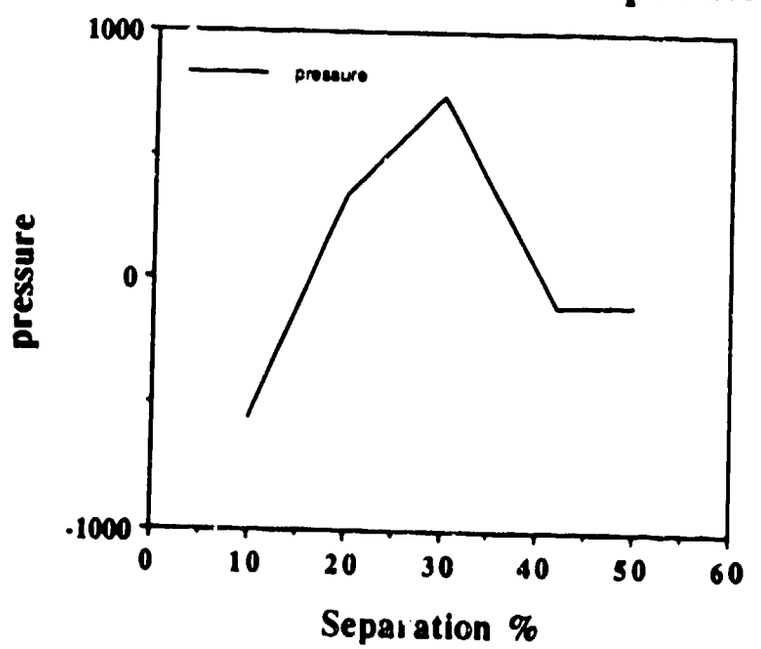


Fig 4: Pressure vs separation

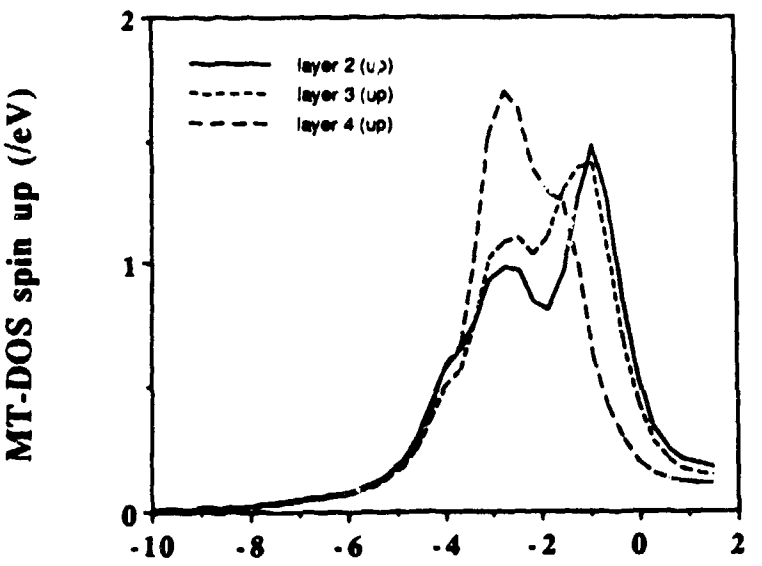


• *Electronic Structure near a (111) grain boundary in Fe*

If all fracture, including environmentally induced embrittlement, is to occur by similar atomistic mechanisms then we may expect that fracture in general is the result of a competition between bonds normal and parallel to a virtual fracture surface. Further, the point of maximum bond strain should be characterized by states crossing E_F, signified by some enhancement in the DOS near E_F, as in the cleavage example discussed above. Extending these ideas, a Fe (111) grain boundary with and without segregated P has been investigated with the LKKR approach. The unrelaxed Σ 3 grain boundary structure which we have examined is formed by joining a stack of (111) planes with its mirror image. The P atoms are placed in the centre of the trigonal capped prisms formed at the grain boundary. This site gives a hard sphere radius to be almost identical to that of the P covalent radius, thus we expect this to be the likely segregation site at this boundary.

In accordance with our conjecture we expect that if P embrittles this (111) boundary then we would find some enhancement of the DOS near E_F on the boundary layer. Accordingly, Fig. 5 shows the DOS for this grain boundary with (Fig. 5b) and without (Fig. 5a) segregated P. There is significant contraction of the d-bands at the boundary which is a direct result of the reduced coordination at the boundary. As a consequence, the magnetic moment is enhanced from the bulk value of 2.2μB to 3.6μB at the boundary layer. Fig 5a shows a small enhancement of the DOS near E_F on the boundary layer in the minority band only. The influence of P on the Fe(111) boundary is shown in (Fig. 5b). The DOS for the interface layer is broken down into P and Fe contributions. On summing these two contributions we find an enhancement in the minority DOS near E_F on the boundary layer (layer 4). There is also significant P-P and Fe-P interactions as evidenced by both the peak at -10eV in the P DOS and the broad band features between 0 and -6eV of E_F. As expected, the influence of the P atoms on the magnetic properties of this boundary is to dramatically reduce the moment to 2.6μB by forming Fe-P bonds. The effect of the P impurities is to form P-P and Fe-P bonds which will be predominantly parallel to the interface, suggesting a weakening of the interface. The overall features of this boundary are similar to those seen in both LKKR and cluster calculations on Ni(210) boundaries both with and without segregated S (7). The analogy with the (100) cleavage of Fe would be the formation of P-P and P-Fe bonds parallel to the boundary that compete with Fe-Fe bonds normal to the boundary. This places a strong constraint on the geometry at a brittle boundary. If we assume that P will occupy the interstices of trigonal capped prisms then a condition for a brittle boundary would be that these trigonal prisms shared edges within the boundary. Thus strain normal to the boundary will create a condition in which the formation of P-P bonds parallel to the boundary complete with the strained Fe-Fe bonds normal to the boundary. Note the formation of the P-P bonds parallel to the boundary will also act to lower the surface energy, thus promoting the tendency for P to embrittle Fe.

Fig 5a: Fe (111) 7 layer grain boundary



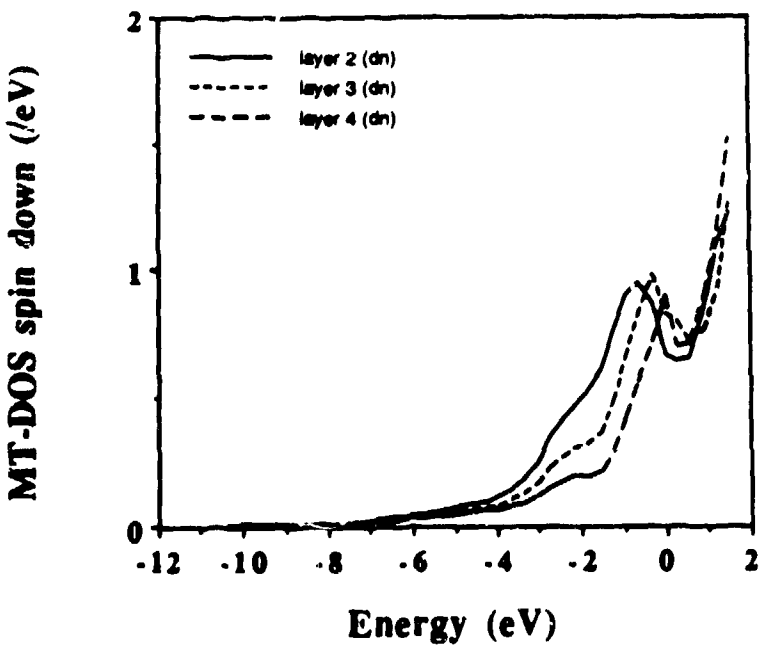
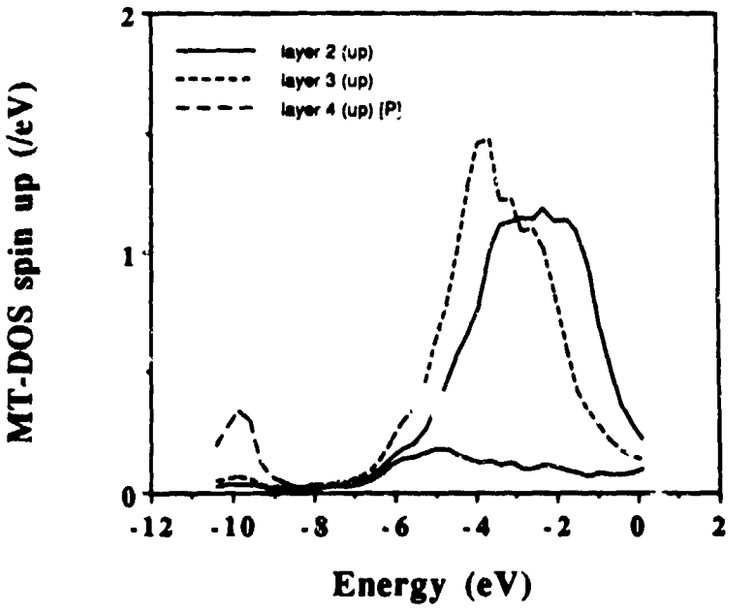
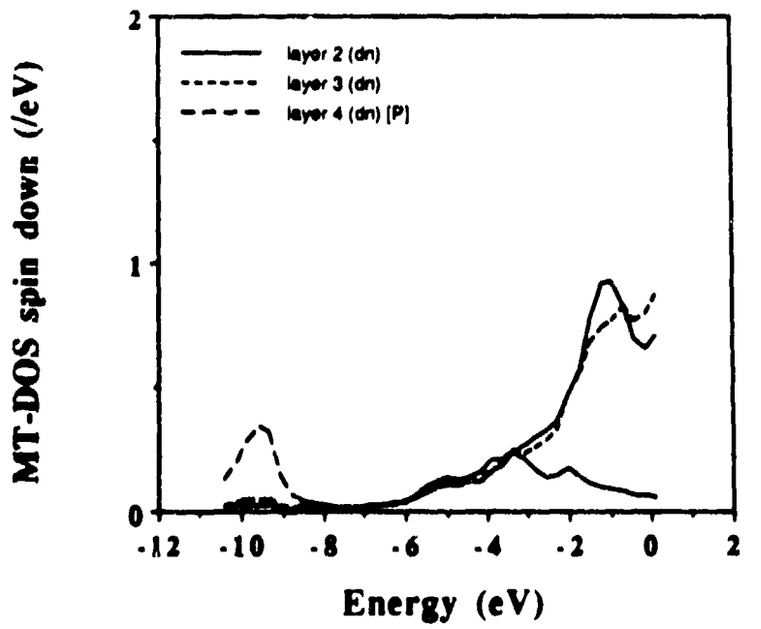


Fig 5b: Fe (111) + P 6 layer grain boundary





CONCLUSIONS

The electronic structure of simple geometries representing an Fe(111) grain boundary and Fe(100) cleavage have been calculated with the spin polarized LKKR technique. In the cleavage calculations we find that the point of inflection in the energy as a function of separartion is close to the point where, by symmetry, the second neighbor bcc bonds at the interface are broken. A signature for this is an enhancement of the electronic DOS near E_F. Calculations are currently underway to test whether a significantly different DOS near E_F can be generated by packing polyhedra containing segregated impurities which either are noninteracting or share corners, edges, or faces. In the grain boundary calculations, we find clear evidence for the formation of both P-P and P-Fe interactions, suggesting the weakening of the interface by preferential bonding in the plane of the interface. A chemical model of strain-induced bond failure is suggested in which impurity-impurity bonds parallel to the fracture surface compete for the cohesive Fe-Fe bonds normal to the surface. Such a situation is conjectured to produce the enhancement of the DOS near E_F consistent with the changes thought to be a prerequisite for brittle failure.

ACKNOWLEDGEMENTS

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