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Electronic Effects of Sulfur in Nickel: A Model for Grain Boundary Embrittlement

by

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ABSTRACT

This paper reports the first study employing detailed electronic structure calculations to investigate a model of grain boundary embrittlement. The results show that adding sulfur to a cluster of nickel atoms causes strong bonds to be formed between the sulfur atom and the nickel atoms nearest to it, while simultaneously weakening bonds between these nickel atoms and their neighboring nickel atoms in the cluster. As a consequence one can suggest that sulfur forms very strong bonds within the plane of the boundary but weakens metal-metal bonds perpendicular to this plane. Although, for the present, the results can be considered only as suggesting one possible embrittling mechanism, they do demonstrate the insight which such calculations can provide into this very central question of grain boundary embrittlement.

INTRODUCTION

Most high purity polycrystalline transition metals composed of a single element do not fail along their grain boundaries (See references listed in Table I). When brittle intergranular fracture is observed, it is the result of the addition of a second element which segregates to the grain boundaries and somehow makes them the lowest energy fracture paths in the material. Numerous examples have been documented and some of them are listed in Table I. In addition to these binary systems, many complex alloys, most notably steels (Briant and Banerji, 1978; McMahon and Marchut, 1978; Edwards, Bishop, Riviere, and Eyre, 1976; Low, Stein, Turkalo, Laforce, 1968; Krahe and Guttman, 1973; Mulford, McMahon, Pope and Feng, 1976) and nickel base super alloys (Holt and Wallace, 1976; White and Stein, 1978; Yamaguchi, Kobayashi, Matsumiya and Hayami, 1979) are quite susceptible to intergranular fracture when specific elements have segregated to their grain boundaries. In most cases, the embrittling elements need only be present in the bulk at concentrations of several hundred parts per million for the occurrence of sufficient grain boundary segregation to cause intergranular fracture. Such concentrations of phosphorus, sulfur, tin and antimony are common in most commercial materials.

Many experimental studies have contributed to our knowledge of which elements segregate to the grain boundaries of the host material and promote embrittlement (see all references given above), what heat treatments enhance or hinder this segregation (see all references given above), and in some cases what remedies prevent or retard the embrittlement (Pichard, Rieu and Goux, 1976; Briant and Banerji, 1979;

McMahon, 1966; McMahon, Cianelli and Feng, 1977). There has been progress also in explaining the mechanics of intergranular crack nucleation and propagation (McMahon, Vitek and Belton, 1978; McMahon and Vitek, 1979). However, throughout all of this research one central question remains unanswered. Why do these elements cause grain boundary embrittlement? It is generally believed that the effect is due to a lowering of the cohesive strength of the boundary which is caused by the segregated element. However, there has been no theoretical work on the electronic structure in such systems to provide supporting evidence for this hypothesis.

In this paper we describe the first results of applying well-known methods previously used in chemical and solid state applications to provide new insight to this key question. The purpose of this paper is threefold. First, to demonstrate the efficacy of molecular orbital theory and the Xα-scattered wave cluster technique to model certain aspects of the grain boundary embrittlement problem; second, to report preliminary results for the nickel sulfur system; and third, to use the results to propose one way in which segregated impurities can weaken the grain boundary.

METHOD

The theoretical method we use to investigate the electronic structure of the local environment at a grain boundary consists of two parts. The first is to use a cluster of atoms to represent the local environment and the second is to use molecular orbital theory to solve for the electronic structure of the cluster of atoms. The method of clusters and molecular orbital theory has previously been applied to a variety of problems: for example, deep defect levels in semiconductors (Messmer and Watkins, 1970; Watkins and Messmer, 1974), chemisorption (Bennett, McCarroll, and Messmer, 1971; Messmer and Salahub, 1977) and magnetic impurities in metals (Johnson, Vvedensky and Messmer, 1979) to mention a few. The selfconsistent field Xα-scattered wave (SCF-Xα-SW) molecular orbital theory (Slater, 1972; Johnson, 1973) has shown itself to be a particularly valuable approach for investigating clusters of atoms, especially for metal clusters (Messmer, Knudson, Johnson, Diamond and Yang, 1976). The great body of published studies over the last five years using the cluster-molecular orbital approach attests to its general efficacy for investigating local electronic structure.

To apply this technique to grain boundaries one first must choose a cluster that in some way resembles the local environment an impurity atom might have if it were at the grain boundary. The choice of such clusters is considerably simplified due to the recent work of Ashby, Spaepen and Williams (1978), who have shown that the structure of grain boundaries in fcc solids can be described in terms of atoms at the vertices of Bernal deltahedra. The individual deltahedra are small clusters containing 4 to 13 atoms and thus provide a natural initial model of local atomic structure with which to investigate the electronic properties by SCF-Xα-SW calculations. In order to investigate the feasibility of applying such methods to this problem we have chosen to use one particular cluster in this work.

The particular cluster we chose is the tetragonal dodecahedron shown in Figure 1. It contains 8 atoms and has D_{2d} point group symmetry. We do not claim that this structure is necessarily a prevalent one in grain boundaries. However, it does contain four atoms (Numbers 1, 2, 3, 4) slightly but symmetrically displaced from the x-y plane and four other atoms farther displaced from this plane. One can roughly consider that the four atoms nearest the x-y plane are grain boundary atoms and that the other four are in the first atomic layers away from the precise boundary.

It is well-established experimentally that sulfur embrittles nickel (Lozinskiy, Volkogon and Pertsovskiy, 1967; Mulford, 1979; Thompson, 1974; Holt and Wallace, 1976). In order to investigate the electronic effects of a sulfur atom at a grain boundary in Ni, we have carried out two calculations on a model system in which the Ni atoms were placed at each of the eight sites of the cluster shown in Figure 1 with an internuclear separation of 2.49 Å. In the first calculation, we considered the cluster containing only the eight nickel atoms. For the second calculation, a sulfur atom was placed at the center of the cluster. An interstitial site of this type is a possible position which a sulfur atom would choose at a grain boundary. For these two configurations we have determined the molecular orbitals for the clusters, their corresponding energy levels, and the valence change densities.

RESULTS AND DISCUSSION

The energy levels for each cluster are shown in Figure 2. We note that in the Ni_8S cluster several of the energy levels have been lowered substantially. Those which have been lowered have orbital wave functions which are highly localized on the sulfur atom and its four nearest neighbors, i.e., the four nickel atoms closest to the x-y plane. Based on this simple analysis one might assume that some Ni-Ni bonds have been weakened.

A better understanding of the bonding may be had if one analyzes the molecular orbitals of the clusters in more detail. Figure 3 shows a set of orbital contours for one set of orbitals. This cross section was taken through the x-z plane. This plane contains two of the nickel atoms nearest the x-y plane plus two of the nickel atoms farther away from the x-y plane. In the Ni_8S cluster it also contains the sulfur atom. In the Ni_8 cluster, bonding interactions are clearly formed between the two types of nickel atoms. However, when the sulfur is added the corresponding orbitals are extremely distorted. More importantly, the bonding interactions between the two types of nickel atoms has been eliminated and replaced by strong bonding interactions between the sulfur atom and the two nearest nickel atoms in this plane.

The two sets of orbitals shown in Figure 3 are representative of those which involve the bonding between the two types of nickel atoms and between the nickel and sulfur atoms. A more succinct picture of the bonding in the cluster can be obtained by summing the orbital charge densities over all the occupied valence orbitals. One can then plot contours of the total valence charge density which exists on any plane. These are shown in Figure 4 for the x-z plane. In this figure we have plotted the same set of contours for both clusters. The three outer-most contours (numbers 1, 2, and 3) in both clusters surround all atoms. However, contour number 4 (which is shown with a heavier line for clarity) is quite different in the two clusters. In Ni_8, it shows bonding between the following nickel atoms, 1 and 7, 7 and 8, 4 and 8, where the characteristic "neck" regions between the pairs of atoms is responsible for bonding. In Ni_8S, the shape of contour number 4 is quite different. The characteristic neck bonding region between atoms 1 and 7, and 4 and 8 is gone, and consequently so is the concomitant strong bonding between the two types of nickel atoms. Furthermore, the size of the neck region between atoms 7 and 8 is reduced from that in Ni_8, implying a weakening of this metal-metal bond as well. Contour 4 in Ni_8S is split into two distinct regions. The upper region of contour 4 and an inner contour of the nickel atoms nearest the sulfur atom enclose both the nickel atoms and the sulfur. This would lead to very strong bonds between this set of nickel atoms and the sulfur. However, there is no such bonding interaction between the sulfur atoms and the other nickel atoms.

From these results a picture clearly begins to emerge. Adding sulfur to the cluster of nickel atoms causes strong NiS bonds to be formed between the nickel atoms nearest the sulfur. Yet this weakens bonds which the nickel atoms would ordinarily have with the other nickel atoms that are not as near the sulfur atom. In this cluster the strong Ni-S bonds involve the sulfur atom and the four nickel atoms nearest the x-y plane. We suggested earlier that these atoms might be thought of as being in the grain boundary. However, the bonds between the nickel atoms nearest the x-y plane and those farther away are weakened. These bonds might represent those from the boundary out to the first layer of the bulk. Clearly, if those are weakened the stress required for fracture would be less.

Therefore, based on the calculations we can suggest an electronic mechanism by which grain boundary embrittlement could occur. We stress that these are only the results from calculations on one system. Furthermore, we have chosen an embrittling element which probably occupies an intersticial site at the grain boundary. Other embrittling elements would clearly be substitutional. Also, many other types of geometrical configurations are possible at the boundary. Yet, with these results, we believe that it is not presumptuous to propose that the above described mechanism is one mechanism by which segregated elements embrittle the grain boundary.

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TABLE 1

HOST ELEMENT	EMBRITTLING ELEMENT	REFERENCE(S)
Cu	Bi	Hondros and McLean, 1974
Cu	Te	Marcus and Paton, 1974
Fe	S	Jolly and Goux, 1969; Pichard, Rieu, and Goux, 1976; Ramasubramanian and Stein, 1973
Fe	P	Ramasubramanian and Stein, 1973
Fe	N	Hopkins and Tipler, 1954
Fe	Sn	Seah and Hondros, 1973
Fe	Te	Rellick, McMahon, Marcus and Palmberg, 1971; Pichard, Rieu and Goux, 1973
Fe	Se	Pichard, Rieu and Goux, 1973
Fe	H	Bernstein and Thompson, 1976
W	P	Joshi and Stein, 1970
Mo	O	Touboul, Minel and Langeron, 1971
Ni	S	Lozinskiy, Volkogon and Pertsovskiy, 1967; Mulford, 1979; Thompson, 1974; Holt and Wallace, 1976

FIGURE CAPTIONS:

Figure 1: The tetragonal dodecahedron

Figure 2: The energy levels for Ni_8 and Ni_8S. The energy levels are denoted by labels of the D_{2d} symmetry point group.

Figure 3: Contours for one set of molecular orbitals (e_1) in the x-z plane. 3(a) is for Ni_8 and 3(b) is for Ni_8S. The x-z plane contains the atoms 1, 4, 7, and 8 in Figure 1 and the S atom in Ni_8S. The contours are linearly increasing in steps of 0.05 a.u. In 3(b) the two x's denote the locations of atoms 7 and 8 which do not contribute to this orbital.

Figure 4: Contours of the total valence charge density in the x-z plane. 4(a) is for Ni_8 and 4(b) is for Ni_8S. The contours are logarithmic, successively increasing by factors of two. The x-z plane contains Ni atoms 1, 4, 7, and 8 from Figure 1 in both clusters and the sulfur atom in Ni_8S. Contour 4, which differs most drastically between the two clusters is drawn more darkly.

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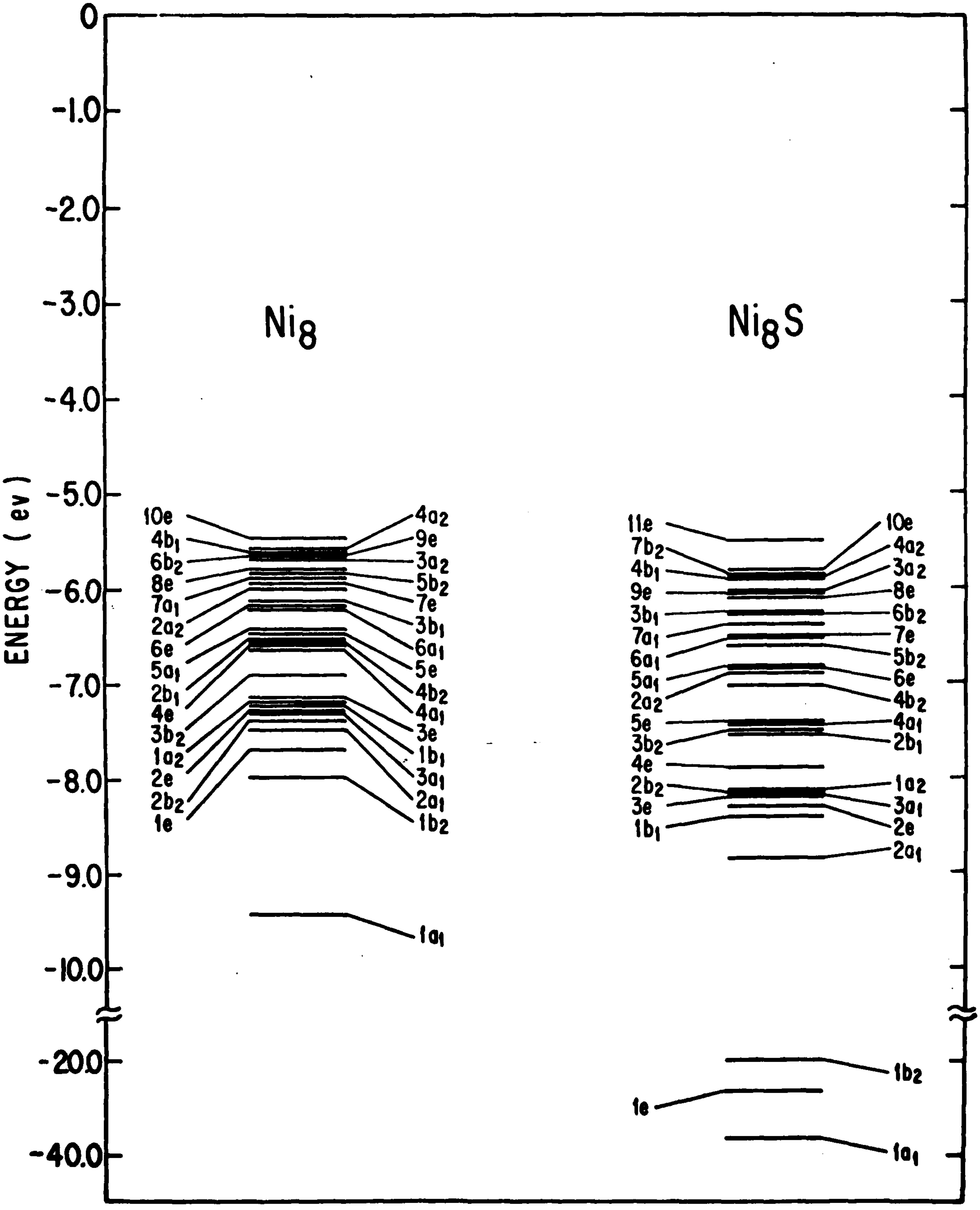
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$5b_2$
7e
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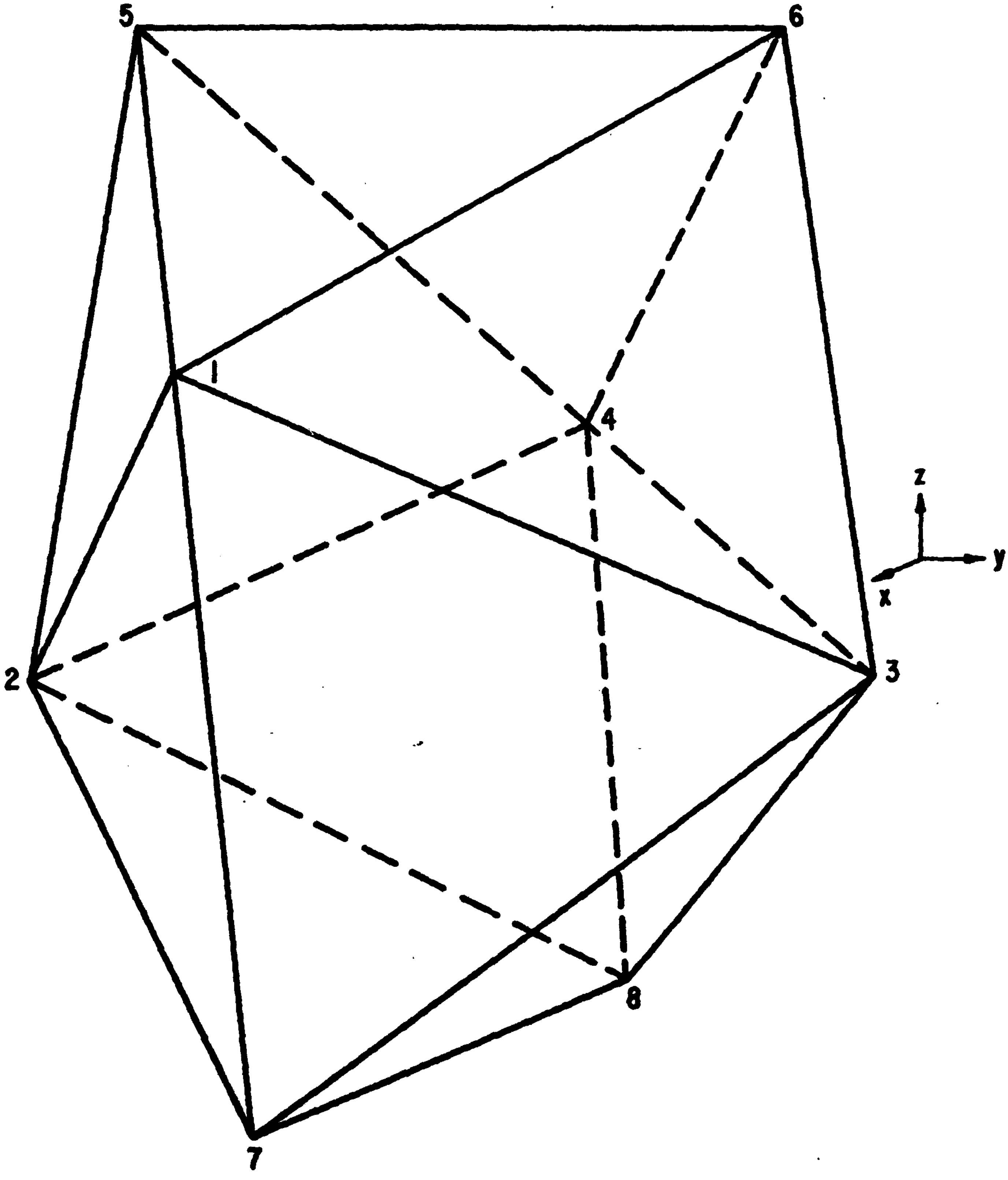
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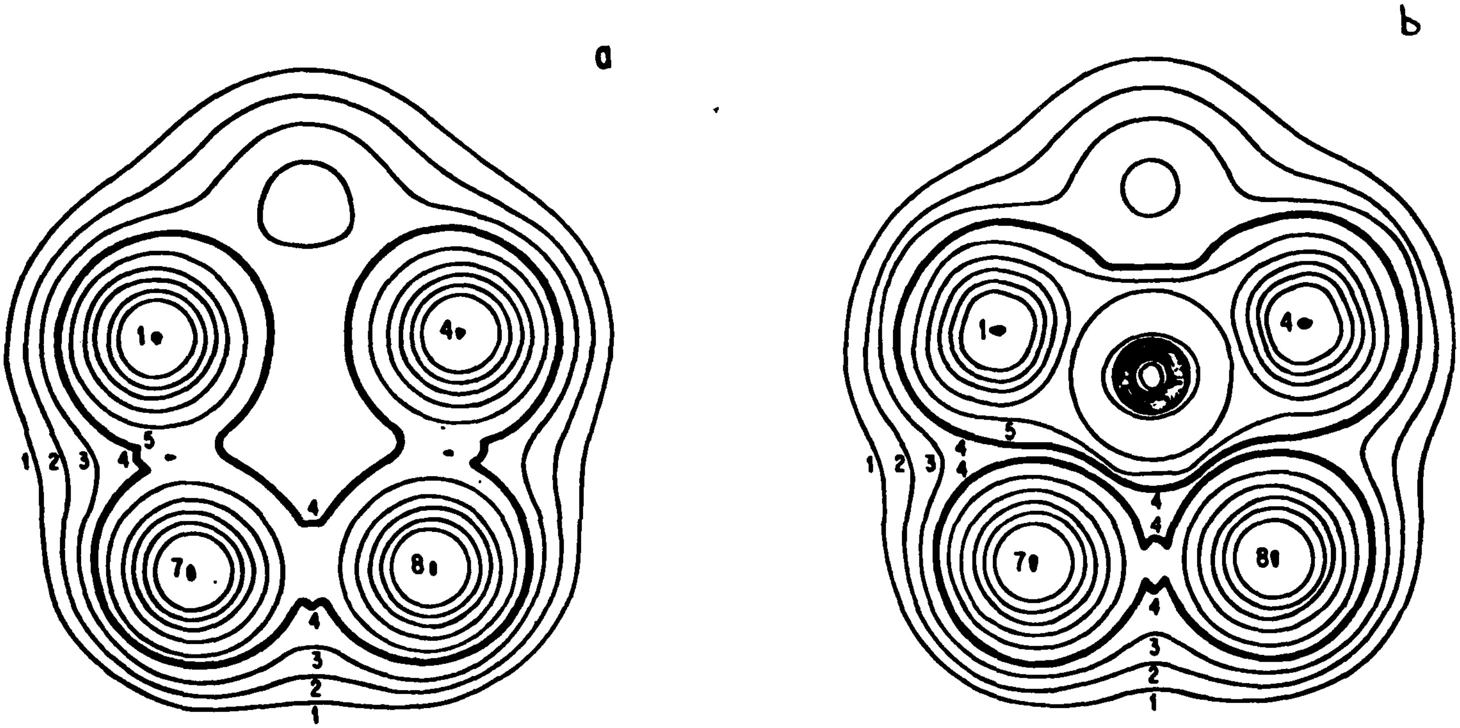

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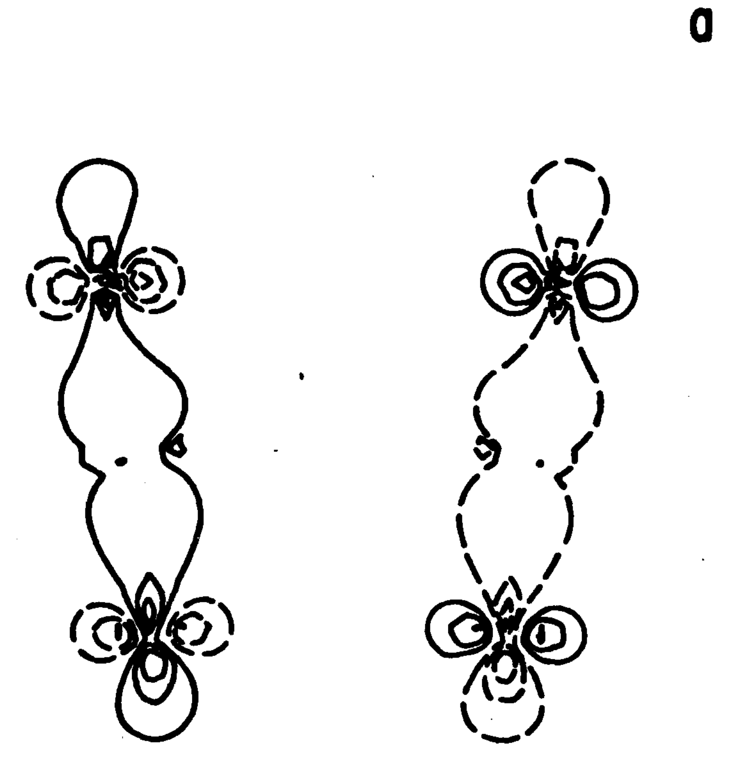

Fig. 2