PHYSICAL REVIEW B VOLUME 29, NUMBER 2 15 JANUARY 1984

Molecular-orbital models of structural phase transformations in crystalline and amorphous cobalt alloys

M. E. Eberhart, R. C. O'Handley, and K. H. Johnson
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 1 November 1983)

Self-consistent-field $X\alpha$ scattered-wave molecular-orbital calculations have been performed on a 19-atom cluster of cobalt. One of the results of this calculation is that a non-space-filling configuration with lower total energy than the hcp structure exists. Furthermore, this stable noncrystalline structure has two nearly degenerate electronic configurations. It is shown that transformations between the two configurations provide a fully consistent model for the recently observed first-order structural phase transformation in cobalt-rich metallic glasses. It is further shown that the structural phase transformation from hcp to fcc crystalline cobalt can be interpreted as resulting from a Jahn-Teller process and is unrelated to the amorphous transformation.

INTRODUCTION

Recently Corb, O'Handley, Megusar, and Grant[1] have observed what appears to be a temperature-dependent, first-order structural phase transformation in a cobalt-rich metallic glass. Though the concept of distinct amorphous phases may at first seem surprising, phase separation[2] and polymorphism[3] have been observed in amorphous metal alloys. Furthermore, noncrystalline condensed phase systems have been successfully modeled as resulting from the packing of non-space-filling structures.[4,5] Consequently, distinct non-space-filling structures could give rise to distinct amorphous phases. Additionally, the preference for a non-space-filling geometry over one that results in a crystal structure is a consequence of a local minimization of free energy.[6] Cluster calculations provide information regarding stability and bonding on a local level, and so provide an ideal vehicle for studying amorphous systems[7] and in particular their possible structural phase transformations.

We will show that the molecular-orbital structure obtained in this calculation on an fcc cluster is not the most stable and that the cluster can lower its total energy by undergoing a Jahn-Teller distortion. The nature of the distortion can be determined by looking at the degenerate wave function at the Fermi energy that enables the Jahn-Teller distortion. The atoms of the cluster will move so as to increase bonding interactions or decrease antibonding interactions while at the same time breaking the degeneracy of the orbital at the Fermi energy. There are two such distortions for this cluster: the first of these is a distortion that will result in a cluster with a symmetry that allows for the formation of the hcp crystalline structure; the second and more stabilizing of the two favors a cluster with a symmetry that is incompatible with any crystalline structure. Clearly the second of these two distortions could only occur in the amorphous phase. We also argue that, when the energy of vibrating nuclei is sufficient to produce an orbital degeneracy at the Fermi energy, a phase transformation will occur. Simple symmetry arguments are used to determine if a vibration of any amplitude is expected to produce such an orbital degeneracy. We begin by analyzing the Jahn-Teller distortions which will stabilize the starting cluster.

CALCULATIONS

A 19-atom cluster was chosen to model the local environment of both crystalline and amorphous cobalt systems. This cluster has the cubo-octahedral configuration of the 12

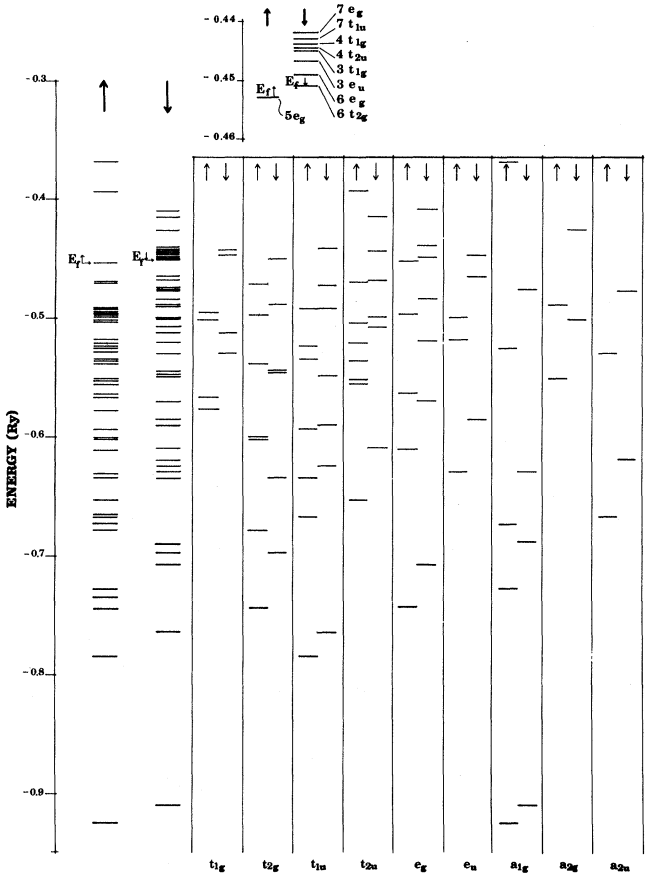

FIG. 1. The energy eigenvalues for the Co_{19} cluster. This calculation was done in spin-polarized mode. The levels at the right are one-electron energy levels corresponding to the spin-up electrons; while the levels to the left correspond to spin-down electrons.

near neighbors and 6 second neighbors in fcc cobalt. This cluster was chosen over other possible configurations because of its high symmetry and because the results of various magnetic measurements on cobalt-rich metallic glasses indicate that the coordination of the cobalt atoms is approximately the same as that observed in crystalline cobalt.[8] Consequently, we expect the subtle changes in local order to be deducible from calculations on any twelvefold-coordinated cluster.

Figure 1 shows the energy eigenvalues resulting from a self-consistent-field $X\alpha$ scattered-wave molecular-orbital (SCF-$X\alpha$–SW MO) calculation on the 19-atom cobalt cluster already discussed. This calculation was carried out in the spin-polarized mode resulting in different energy eigenvalues for the spin-up and spin-down levels. The difference in occupancy of the spin-up and spin-down levels results in a net excess of 29 electrons in the spin-up levels. This represents a bohr magneton number of 1.52 per Co atom. fcc (Ref. 9) and hcp (Ref. 10) cobalt both have a magnetic moment $1.7\mu_B$ per Co atom;[9] this value includes orbital and conduction-electron contributions to the magnetic moment. Measurements of the orbital contributions indicate a $3d$ spin moment of $1.56\mu_B$ per Co atom.[11] The bandwidth resulting from our calculation is 95% of that obtained from band-structure calculations which agree well with experimentally determined density of states.[11] These results indicate that this 19-atom cluster is a remarkably fine model for densely packed Co.

RESULTS

The ground state

The triply degenerate $6t_{2g}$ (Fig. 1) orbital is the highest occupied molecular orbital and has a partial occupancy of one electron. The cluster can therefore lower its total energy by undergoing a Jahn-Teller distortion which reduces its symmetry to eliminate the degeneracy at the Fermi level. This distortion must be accomplished by minimizing antibonding and/or maximizing bonding interactions of the $6t_{2g}$ orbital. Figure 2 shows a contour plot of the $6t_{2g}$ orbital in a [100] plane. This orbital is antibonding between the central cobalt atom and its first coordination sphere; all other interactions are very weak and nonbonding. The distortion that will result in lowering the total energy of this cluster will, therefore, be one that will weaken the first-neighbor antibonding interactions. While a dilation of the cluster would weaken these antibonding interactions this distortion does not lower the symmetry of the cluster and, therefore, does not remove the degeneracy at the Fermi energy. Such a distortion, therefore, would not be a Jahn-Teller distortion.

Figure 3 shows a three-dimensional representation of the bonding between the central cobalt atom and the first neighbors in the $6t_{2g}$ orbital. This figure is drawn to emphasize that the 12 lobes of the d_{xy}, d_{xz}, and d_{yz} orbitals on the central cobalt atom point toward the 12 nearest neighbors (the vertices of a cubo-octahedron), with the lobes of one phase (positive or negative) lying in a plane terminating at the vertices of a regular hexagon while the lobes of the other phase terminate at the vertices of a triangular antiprism.

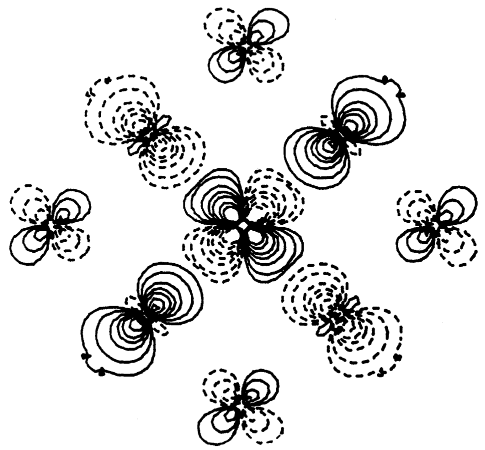

FIG. 2. A contour plot of the $6t_{2g}$ orbital in the xy plane (all perpendicular planes are equivalent). The dotted lines indicate the negative phase of the wave function.

Figure 3 shows that the eight triangular faces of the cubo-octahedron formed by the d lobes on the central cobalt atom are of two types: one type (two faces) in which the lobes are all of the same phase (homophasic), and the other type (six faces) in which the lobes are of different phases (heterophasic). Certain rotations of three first neighbors off one of these eight triangular faces can result in a lessening of the antibonding interaction in the $6t_{2g}$ orbital. (Throughout this paper we refer to symmetry-lowering distortions as rotations. This is not meant to imply that these rotations are the required paths for a transformation, rather only that a rotation will carry the atoms to the correct low-energy positions.) However, depending on the type of the triangular face normal to which the rotation is occurring, there will be two very different types of stabilization. The

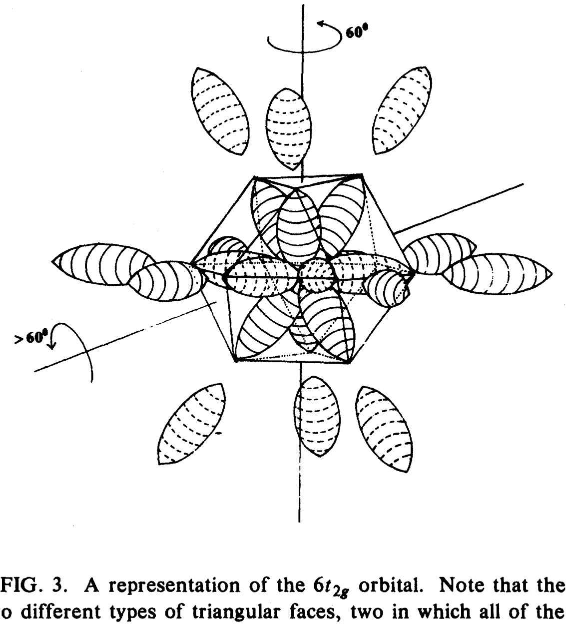

FIG. 3. A representation of the $6t_{2g}$ orbital. Note that there are two different types of triangular faces, two in which all of the lobes are of the same phase, and six in which the lobes are of different phases.

rotation shown in Fig. 3 for one of the two homophasic faces will stabilize the cluster by diminishing three antibonding interactions. The rotation of this type that will maximally stabilize this cluster is a 60° rotation. The resulting molecular orbital will be one in which the lobes on the triangular plane of atoms off one of the two end faces of the triangular antiprism have been rotated to a position in which they are staggered with respect to the lobes on the central cobalt atom. The resulting configuration is representative of hcp cobalt; the weakening of antibonding interactions accompanying the rotation will lead to a contraction along the *c* axis, as is observed in hcp cobalt, and result in a c/a ratio of less than 1.63. We believe that this Jahn-Teller distortion accounts for the relative stability of hcp cobalt over fcc.

A rotation about one of the six heterophasic faces will again lessen three antibonding interactions; however, in this case the rotation will also result in the formation of two bonding interactions. The rotation that leads to the maximal stabilization of the cluster is no longer a 60° rotation because a greater rotation willl strengthen two bonding interactions. The most stable rotation will be one that minimizes the total energy of the one antibonding and two bonding interactions, and can be shown by simple arguments to be between 60° and 120°, $60° + \delta$. (This rotation will be indistinguishable from a rotation of between 0° and 60°.)

Because this non-60° rotation results in the formation of two bonding interactions as well as diminishing three antibonding interactions off each of the six faces, it is probably more stable than the rotation that simply reduced antibonding interactions off each of two faces. However, δ not equal to zero will destroy the threefold axial symmetry of the bonding off these heterophasic faces; the two atoms forming bonding interactions will be drawn toward the central cobalt atom more so than the atom still subject to antibonding interactions. The resulting cluster will be one with a symmetry that does not fill space and therefore will not occur in crystalline cobalt. That a rotation for which δ does not equal zero is indeed more stable than the space-filling 60° rotation is suggested by the fact that in isolated inorganic molecules this partial rotation has been observed.[12] In Co(II) ions coordinated by the hexadentate ligand *Pcc* BF, the rotation angle is 58° ($\delta = \pm 2°$). This is a highly rigid ligand which should favor the trigonal prismatic conformation; the small Jahn-Teller induced rotation is most remarkable. Other less rigid hexadentate ligands such as $(py)_3$tach, $(py)_3$tame, and $(py)_3$tren show an increasing deviation from the trigonal prismatic coordination, respectively, while still not adopting the octahedral coordination. Thus we believe this non-space-filling distortion of the cluster to be one mechanism stabilizing the amorphous state.

Figure 4 shows the calculated eigenvalues for the fcc cluster and the estimated relative energies of the orbitals near the Fermi energy for its two derivative structures discussed above. The levels resulting from the hcp distortion of the starting cluster are shown to the left of Fig. 4 while the results of the crystalline-incommensurate rotation are shown to the right. The distortion that leads to the hcp structure reduces the symmetry of the cluster to D_{3h} and splits the t_{2g} orbital into ones with symmetry of a_1' and e' while the original e_g orbital is unchanged, being designated an e'' orbital in the new symmetry. We estimate this $e' - a_1'$ splitting from the temperature of the crystalline hcp to fcc transformation.

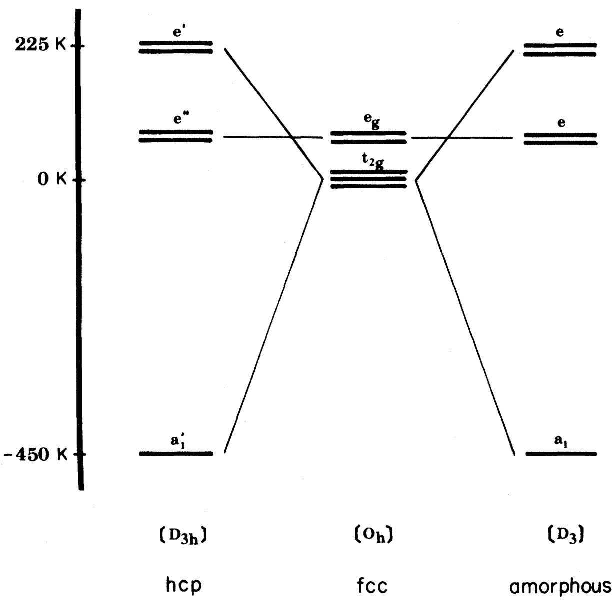

FIG. 4. Center: nearly degenerate e_g and t_{2g} levels near the Fermi energy calculated for the fcc cluster. The t_{2g} levels are occupied by only one electron. Left and right: The estimated positions of the energy-level shifts near E_F as a result of the proposed Jahn-Teller distortions. A more stabilizing Jahn-Teller than D_{3h} distortion is possible and results in the crystalline incommensurate structure of nearly D_3 symmetry (see text). The $e' - a_1'$ splitting for D_{3h} symmetry is estimated from the temperature (400 °C) for the hcp to fcc transformation.

The incommensurate rotation, shown to the right of Fig. 4, destroys all the symmetry of the original cluster, but for the sake of clarity we will refer to the resulting structure as nearly D_3 and thus the t_{2g} orbital at the Fermi energy can be estimated to be split into an a_1 and an e orbital. The e_g orbital in the original cluster again is unsplit and becomes an e orbital in the reduced symmetry. The original e_g orbital will be unaffected by either rotation and is therefore located approximately 465 K above the highest occupied molecular orbital (HOMO), as per the calculation on the 19-atom cluster.

Phase transformations

As we discuss elsewhere,[13] a phase transformation can occur only when a vibration induces a degeneracy at the Fermi energy. Briefly, when the energy of some vibrational mode is equivalent to the energy saved as a result of molecular-orbital splitting, in this case the Jahn-Teller splitting, then the total energy of the cluster is no longer lowered by a distortion. One can show that this is the maximum energy that can be stored in this mode. Consequently, the energy of this mode must be converted to potential energy by restoring the cluster to its high-symmetry configuration before the temperature can be increased. One can find this point in the one-electron approximation by modeling the cluster at the end points of a molecular vibration. Here all of the kinetic energy of this particular vibrational mode has been stored as potential energy in the electronic wave functions.

When the energy of the molecular vibration is equal to that saved by the molecular-orbital splitting, solutions to the one-electron electronic Hamiltonian will result in a degeneracy at the Fermi energy. The problem of calculating transformation temperatures can be reduced to finding the vibrations necessary to produce a degeneracy at the Fermi energy. We begin with the phase transformations that are anticipated for the hcp structure as the temperature is increased.

Inspection of Fig. 4 will show that the first degeneracy anticipated as a result of vibrational distortion is one between the a_1' and the e'' orbitals of the D_{3h} cluster. However, inspection of correlation tables[14] indicates that it is impossible to produce a symmetry-required degeneracy (as long as we restrict ourselves to one of the 32 crystallographic point groups) between these two orbital. The next possible degeneracy would be one between the a_1' orbital and the e' orbital. The vibration that results in a degeneracy between these two orbitals is one that results in a cluster symmetry of O_h, i.e., a vibration that negates the initial Jahn-Teller distortion. We believe that this is the process that leads to the hcp to fcc transformation. (It is for this reason that the e'-a_1' splitting, and not the e''-a_1' splitting, was approximated as 675 K.)

More direct arguments suffice to explain the phase transformations in the amorphous states. In the cluster with nearly D_3 symmetry resulting from the crystalline incommensurate Jahn-Teller distortion the first possible degeneracy is between the a_1 and the e orbital. It is no longer required that we restrict ourselves to crystallographic point groups. A vibration that results in a local icosahedral symmetry (I or I_h) allows a degeneracy between these two orbitals.[15] By dilating the resulting cluster with I or I_h symmetry so as to adjust relative bonding interactions, it will always be possible to produce a degeneracy between the a_1 and the e orbital. These observations lead to the suggestion that at about 450 K a vibration of sufficient amplitude carries the crystalline incommensurate cluster with nearly D_3 symmetry into another crystalline incommensurate cluster with I or I_h symmetry. We believe that this is the first-order amorphous structural phase transformation that has been observed.

In contrast to the model proposed so far for this amorphous transformation,[1,16] our calculations indicate that the electronic mechanism for the transformation is not the same as that which promotes the hcp to fcc transformation in crystalline cobalt. Rather, a different orbital degeneracy was required in the amorphous phase. Our calculation therefore suggests that not all substances which undergo crystalline solid-solid phase transformations will have corresponding phase transformations in their amorphous counterparts.

ACKNOWLEDGMENTS

Sponsorship of this research by the U.S. Army Office of Research and the National Science Foundation is gratefully acknowledged.

---

[1] B. W. Corb, R. C. O'Handley, J. Megusar, and N. Grant, Phys. Rev. Lett. 51, 1386 (1983).

[2] C. P. Chou and D. Turnbull, J. Non-Cryst. Solids 17, 169 (1975); L. E. Tanner and R. Ray, Scr. Metal. 657 (1980).

[3] D. S. Lashmore, L. H. Bennett, H. E. Schone, P. Gustafson, and R. E. Watson, Phys. Rev. Lett. 48, 1760 (1982).

[4] M. E. Eberhart, K. H. Johnson, and R. C. O'Handley, in *Rapidly Solidified Amorphous and Crystalline Alloys*, edited by B. H. Kear and B. C. Giessen (Elsvier, New York, 1982).

[5] J. F. Sadoc, J. Non-Cryst. Solids 44, 1 (1981); P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. Lett. 47, 1297 (1981).

[6] F. C. Frank, Proc. R. Soc. London, Ser. A 215, 43 (1952).

[7] R. P. Messmer, in *Metallic Glasses*, edited by F. E. Luborsky (Butterworth, London, 1983).

[8] B. W. Corb, R. C. O'Handley, and N. J. Grant, Phys. Rev. B 27, 636 (1983).

[9] J. F. Janak and A. R. Williams, Phys. Rev. B 14, 4199 (1976).

[10] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 465.

[11] F. Batallan and I. Rosenman, Phys. Rev. B 11, 545 (1975).

[12] K. F. Purcell and J. C. Kotz, *Inorganic Chemistry*, (Saunders, Philadelphia, 1977), p. 602.

[13] M. E. Eberhart and K. H. Johnson (unpublished).

[14] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[15] The only degeneracy that could occur as a result of a vibration is an accidental degeneracy. While symmetry arguments alone are not sufficient to predict if an accidental degeneracy can occur, inspection of the e_g wave function of the O_h cluster leads us to believe that such an accidental degeneracy would be unlikely.

[16] R. C. O'Handley, B. W. Corb, J. Megusar, and N. J. Grant, in the Proceedings of the Liquid and Amorphous Metals V Conference, UCLA, 1983 [J. Non-Cryst. Solids (to be published)].