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STERIC PROPERTIES OF THE
TRANSITION-METAL IONS ON STEPPED SURFACES

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ABSTRACT

We present simplified model calculations for the steric properties of the transition-metal ions in various crystalline geometries on stepped surfaces. Results derived from these calculations are consistent with available experimental data of catalytic properties of Pt and Au stepped surfaces.

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I. INTRODUCTION

Surfaces of crystals characterized by high Miller indices consist of terraces of low index planes separated by steps often one atom in height. There is experimental evidence that these atomic steps play an important role in enhancing catalytic reactions in Pt (Lang, Joyner and Somorjai, 1972). In particular, Somorjai, Joyner and Lang (1972) have shown that dissociative adsorption of diatomic molecules and aromatic hydrocarbons occur more readily on these stepped surfaces than on the low index planes of Pt, which is one of the best catalysts for a variety of surface chemical reactions. Gold, the neighbor to platinum in the periodic table is relatively inert; none of the common adsorbates, including oxygen, have been found to chemisorb on Au at room temperature. Chesters and Somorjai (1975) investigated the activity of both a low index (111) Au surface and a high index Au surface with (111) terraces in the chemisorption of oxygen and hydrocarbons at room temperatures and above. They found that the oxide forming characteristics of the low index (111) and the high index stepped crystal faces of Au were identical. Furthermore, under low pressure conditions and below 550°C, the stepped Au surface remains

inert to adsorption of the light hydrocarbon molecules, just as the Au (111) crystal face. These experimental results indicate that surface steps play no appreciable role in altering chemical reaction characteristics in Au surfaces, whereas the steps definitely play a catalytic role in the case of Pt surfaces.

One would expect the local field experienced by a transition-metal ion arising from (1) the self-consistent field of the itinerant s electrons and (2) the crystal field from the lattice, to be different depending on the ion's position: in the bulk, on the planar surface or near a step corner. This local field has two major effects: (1) causing a sizeable d-electron transfer from the step corner to the bulk or vice versa, and (2) producing different d-orbital level splittings and different d-orbital occupations, depending on the position of the metal ion. These effects indicate that atomic positions near surfaces and step corners are important in determining the chemical signature of the atom and consequently different chemical reactions may be favored at surface step sites. In this paper, we have made a systematic study of the above mentioned effects of the local field in the transition-metals of the iron series. Our results clearly display different stereochemistry for different geometries in a metal surface;

and when applied specifically to Pt and Au, our conclusions are consistent with the experimental results.

II. FORMULATION

Transition-metals are especially hard to treat theoretically because of the presence of both s-like and d-like states in the conduction band. The free electron theory works well for the s-like part of the wavefunction but a tight-binding model is needed to account for the atomic-like correlations for the d-like part of the wavefunction. We choose to treat the s-electrons as completely free and the d-electrons as localized and atomic-like. This approximation removes entirely the s-d hybridization and would have given unrealistic results for the electronic structure, but for our purpose here of determining the chemical signature of the surface atoms, the essential physics is not lost with this approximation.

The d-electron transfer as a result of the local field is handled as follows:

(a) Starting with Kesmodel and Falicov's (1975) solution of the electronic potential arising from the s-like electrons confined in a 90° metal wedge, metal ions with their localized d-electrons are placed into the lattice. Then

the zeroth order electron transfer will be

$$\Delta N^0(\underline{r}) \approx N(\epsilon_F) \times \Delta V(\underline{r}) \quad , \quad (2.1)$$

where $\Delta V(\underline{r})$ is the electronic potential at $\underline{r}$ with respect to that in the bulk and $N(\epsilon_F)$ is the bulk electronic charge density at the Fermi level.

(b) The s-like conduction band is allowed to act as a reservoir for the charge transfer $\Delta N^0(\underline{r})$.

(c) The initial transfer of charge $\Delta N^0(\underline{r})$ at one site creates a new perturbation potential at neighboring sites which can in turn produce a further charge transfer $\Delta N^1(\underline{r})$, the first order correction to $\Delta N^0(\underline{r})$. Higher order corrections should be included until a self-consistent result is reached.

(d) Kesmodel and Falicov's potential (1975) shows a maximum electronic potential of ~0.38 eV located at the corner at 1.1Å from each edge for tungsten. For corner geometries bounded by different edges, we find that the corner atom invariably [with a reasonable allowance of 5-10% (Tsang and Falicov, 1975) for lattice relaxation] falls on the potential maximum and that all other neighbors are situated already at electronic potentials close to the bulk value of zero. Furthermore, the s-electron density is high

enough that the static screening is effective even at the corner so that the perturbation potential as a result of the initial charge transfer is almost completely screened at one lattice constant away.

(e) As a result, the first order correction to $\Delta N^0(\underline{r})$ may be neglected and it is adequate to assume for the outermost corner atom, electrons get "transferred out" by

$$\Delta N(\underline{r}) \approx N(\epsilon_F) \times \Delta V_{\max} ; \quad (2.2)$$

and for all other atoms, $\Delta N(\underline{r})$ to be zero. Taking the value $\Delta V_{\max} = 0.38$ eV for W (Kesmodel and Falicov, 1975) as a typical value, a knowledge of the Fermi level bulk electronic density of states for various transition-metals gives the measure of the d-electron transfer.

Given the number of localized d-electrons on a metal ion, the local field produces level splittings of the many electron ground states determined by Hund's rule for a free metal ion. Splittings caused by the crystal field alone are at least twenty times larger than that caused by the potential arising from the s-like electrons given by Kesmodel and Falicov (1975). Therefore, to the zeroth order, only crystal field effects need to be included in determining the occupation of the d-orbitals for metal ions at various surface

geometries. A scheme to study systematically the stereochemistry of metal ions at various surface geometries within our approximation emerges as follows:

(1) We choose across the periodic table ions with different number of d-electrons, namely: $V^{++}(3d^3)$, $Cr^{++}(3d^4)$, $Fe^{++}(3d^6)$, $Co^{++}(3d^7)$, $Ni^{++}(3d^8)$, and $Cu^{++}(3d^9)$. The ionized electrons are assumed to be all in the conduction band and the d-electrons on the ions are assumed to be atomic-like. The 3d series is chosen for their small s-d hybridization and small spin-orbit coupling (with reference to the lattice crystal field splitting); then the many electron states are specified by the total orbital momentum L and total spin momentum S . The respective many states determined by Hund's rule for these free ions in the absence of crystal field are: $^4F(V^{++})$, $^5D(Cr^{++})$, $^5D(Fe^{++})$, $^4F(Co^{++})$, $^3F(Ni^{++})$, and $^2D(Cu^{++})$. These states have an orbital degeneracy of order $(2L+1)$, so the D states are five-fold degenerate and the F states are seven-fold degenerate.

(2) Fig. 1 shows the step geometries chosen: Vanadium and Cr crystallize in the bcc structure and the step chosen is bound by the perpendicular planes $(\bar{1}\bar{1}0)$ and $(1\bar{1}0)$. Nickel and Cu have the fcc structure, Fe and Co crystallize in different structures, for this calculation we choose the fcc phase for both Fe and Co. The step chosen for the fcc structure

shown in Fig. 1 is bound by the orthogonal planes (001) and (010). The label S refers to the atoms on the step terrace and the labels C_1 and C_2 denote the atoms at the step corner. The Cartesian axes $\hat{x}$, $\hat{y}$, $\hat{z}$ are chosen so that in both the fcc and bcc geometries the step terraces lie in the x-y plane and the step ledges in the y-z plane.

(3) The point-charge ionic model is used in determining the energy levels of the d-electrons at the different sites S, C_1 and C_2 when the crystal field is turned on. The crystal field theory is by now well established and has been widely applied in paramagnetic resonance calculations; several reviews exist in the literature (Hutchings, 1964; Abragam and Bleaney, 1970). If $\mathcal{H}_0$ is the Hamiltonian of the free ion, then the Hamiltonian $\mathcal{H}$ of the ion in a crystalline environment has the form $\mathcal{H} = \mathcal{H}_0 + V'$, where V' is the perturbation potential which has the symmetry of the surroundings of the ion in question

$$V'(\underline{r}) = \sum_j \frac{q_j}{|\underline{r} - \underline{R}_j|}, \quad (2.3)$$

where q_j is the charge at the j^{th} nearest-neighbor ion, a distance R_j from the origin, site of the metal ion in question. The level splittings and the new ground state in the presence of a crystal field is obtained by diagonalizing the

matrix $\langle \Psi_0 | V'(\underline{r}) | \Psi_0 \rangle$, where Ψ_0 is the $(2L+1)$ degenerate ground state $|L, M_L\rangle$ to $\mathcal{H}_0$. To evaluate actually the matrix elements, $V'(\underline{r})$ is first expanded in spherical harmonics and then their "Operator Equivalents" are obtained (Stevens, 1952; Racah, 1942; Buckmaster, 1962). The "Racah Operator Equivalents" we used are angular momentum operators $\tilde{O}_{\ell m}$ which transform in the same way as the spherical tensors $\frac{4\pi}{(2\ell+1)} Y_{\ell m}(\theta, \phi)$. Smith and Thornley (1966) listed these operators up to $\ell=6$ and give a general expression for their matrix elements between angular momentum eigenstates. Symmetry considerations alone reduce the otherwise infinite series expansion of $V'(\underline{r})$ to only a few terms. Expressed in terms of the "Racah Operator Equivalents" $\tilde{O}_{\ell m}$, the various crystal field potentials at different geometries (S, C_1 and C_2 respectively) for the fcc structure are found to be:

$$V_S(\underline{r}) = \frac{8q}{a} - \frac{q}{a} \alpha_J \langle r^2 \rangle \tilde{O}_{20} + \frac{q}{a} \beta_J \frac{\langle r^4 \rangle}{a^4} \left[-\frac{1}{8} \tilde{O}_{40} - \frac{3}{16} \sqrt{70} (\tilde{O}_{44} + \tilde{O}_{4-4}) \right], \quad (2.4)$$

$$V_{C_1}(\underline{r}) = \frac{6q}{a} + \frac{q}{a} \beta_J \frac{\langle r^4 \rangle}{a^4} \left[-\frac{7}{8} \tilde{O}_{40} - \frac{\sqrt{70}}{16} (\tilde{O}_{44} + \tilde{O}_{4-4}) \right], \quad (2.5)$$

and

$$\begin{aligned}
 v_{C_2}(\underline{r}) = & \frac{11q}{a} + \frac{q}{a} \alpha_J \frac{\langle r^2 \rangle}{a^2} \left[-\tilde{O}_{20} + \frac{\sqrt{6}}{4} (\tilde{O}_{21} - \tilde{O}_{2-1}) - \frac{\sqrt{6}}{8} (\tilde{O}_{22} - \tilde{O}_{2-2}) \right] \\
 & + \frac{q}{a} \beta_J \frac{\langle r^4 \rangle}{a^4} \left[-\frac{43}{32} \tilde{O}_{40} + \frac{\sqrt{5}}{16} (\tilde{O}_{41} - \tilde{O}_{4-1}) - \frac{5\sqrt{10}}{32} (\tilde{O}_{42} + \tilde{O}_{4-2}) \right. \\
 & \left. + \frac{\sqrt{35}}{16} (\tilde{O}_{43} - \tilde{O}_{4-3}) - \frac{9\sqrt{70}}{64} (\tilde{O}_{44} + \tilde{O}_{4-4}) \right] , \quad (2.6)
 \end{aligned}$$

where a is the nearest-neighbor distance and q is the same charge on each neighbor; $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are radial averages for the 3d ions, their values are tabulated in Abragam and Bleaney (1970); α_J and β_J are numerical factors that come in as the potentials are transformed into "Operator Equivalents," they are functions of the quantum numbers L and S and the number of d-electrons on the ion, their values are tabulated in Hutchings (1964). The first term in each of the Eqs. (2.4), (2.5) and (2.6) account for the number of nearest neighbors present in the various geometries, actual d level splittings will only arise from the other terms.

For the bcc structure, the crystal field potentials expressed in terms of the "Operator Equivalents" are:

$$\begin{aligned}
 v_S(\underline{r}) = & \frac{6q}{a} + \frac{q}{a} \alpha_J \frac{\langle r^2 \rangle}{a^2} \left[\sqrt{\frac{2}{3}} i (\tilde{O}_{22} - \tilde{O}_{2-2}) \right] \\
 & + \frac{q}{a} \beta_J \frac{\langle r^4 \rangle}{a^4} \left[-\frac{7}{8} \tilde{O}_{40} + 2 \frac{\sqrt{10}}{9} i (\tilde{O}_{42} - \tilde{O}_{4-2}) - \frac{1}{3} \sqrt{\frac{35}{2}} (\tilde{O}_{44} + \tilde{O}_{4-4}) \right] \quad (2.7)
 \end{aligned}$$

$$V_{C_1}(\underline{r}) = \frac{4q}{a} - \frac{q}{a} \frac{\langle r^4 \rangle}{a^4} \beta_J \left[\frac{14}{9} \tilde{O}_{40} + \frac{\sqrt{70}}{9} (\tilde{O}_{44} + \tilde{O}_{4-4}) \right] \quad (2.8)$$

$$V_{C_2}(\underline{r}) = 2V_{C_1}(\underline{r}) . \quad (2.9)$$

We utilize matrix elements $\langle LM_L | \tilde{O}_{\lambda m} | LM'_L \rangle$ tabulated by Birgeneau (1967) to set up the matrices $\langle \Psi_0 | V'(\underline{r}) | \Psi_0 \rangle$ for diagonalization. The resultant d-level splittings of the free ion ground state in various surface geometries (surface site S, corner sites C_1 and C_2) are given in Table 2 in terms of the cubic crystal field parameter $10Dq$; values of $10Dq$ for the different ions are taken out from Abragam and Bleaney (1970, p. 378) and listed in Table 1. In Table 2, the energy levels of the excited states are given with respect to the ground state of each configuration; the degeneracy of each state is also given.

(4) The new many electron ground state Ψ in each particular crystalline environment is of primary interest. The angular part of these new ground states in different geometries is given in Table 3. These many electron states are expressed in terms of spherical harmonics $Y_{Lm_L} = |Lm_L\rangle$ where L is still the total orbital momentum quantum number in a free field. For the ion with N equivalent electrons, we may define the function

$$\rho(\underline{r}) = \sum_{i=1}^N \int |\Psi(\underline{x}_1, \underline{x}_2, \dots, \underline{x}_i \dots \underline{x}_N)|^2 \delta(\underline{r}-\underline{x}_i) d^3x \quad (2.10)$$

which is the probability of finding an electron at $\underline{r}$. To evaluate $\rho(\underline{r})$, each many electron ground state must be expanded into functions of determinantal product states involving single electron orbitals; the decomposition of $|Lm_L\rangle$ into their constituents $|\ell_1 m_{\ell_1}, \ell_2 m_{\ell_2}, \dots, \ell_N m_{\ell_N}\rangle$ is guided by Clebsch-Gordon coefficients. The resultant angular distribution of $\rho(\underline{r})$ in the three orthogonal planes as defined in Figure 1: (1) x-z plane; (2) y-z plane, that of the step ledge; and (3) x-y plane, that of the step terrace, will clearly demonstrate the steric properties of an ion when it is placed at different sites near the surface.

III. RESULTS AND DISCUSSION

The d-electron wave function is a product of the radial and the angular part; assuming the radial part to be constant, we display the resultant constant contour of the angular part of $\rho(\underline{r})$ plotted in the three planes for the ions V^{++} , Cr^{++} , Fe^{++} , Co^{++} , Ni^{++} and Cu^{++} in Figs. 2-7, respectively. For the

ions with more than half-filled d-shells: $\text{Fe}^{++}(3d^6)$, $\text{Co}^{++}(3d^7)$, $\text{Ni}^{++}(3d^8)$ and $\text{Cu}^{++}(3d^9)$, the many electron wavefunction is decomposed into hole orbitals rather than electron orbitals so that the $\rho(r)$ displayed in Figs. 4-7 corresponds to the probability of finding a hole at any given angular position. These figures clearly indicate that the stereochemistry of a corner atom can be quite different from that of a surface atom, therefore, a different kind of bonding is favored at different sites. We would like to apply these results qualitatively to the transition-metals of the 5d series, specifically to Au and Pt.

Gold crystallizes in the fcc structure and its atom has the electronic configuration $(\text{Xe})6s^1(5d)^{10}$. The bulk optical density of states at the Fermi level $N(\epsilon_F) \sim 0.3$ electron/eV-atom (Krolikowski and Spicer, 1970), then the zeroth order maximum charge transfer from the "outermost corner" atom C_1 will be $\sim (0.38\text{eV} \times 0.3)\text{electron/eV-atom} \sim 0.1$ electron. This charge transfer is negligible. Then the atoms on corner sites as well as the atoms on low index step terraces have a nearly filled d-shell which implies non-reactivity in chemical reactions. This is consistent with the experimental findings that steps seem to play no significant role in enhancing reactivity.

Platinum also crystallizes in the fcc structure and its electronic configuration is $(\text{Xe})6s^1(5d)^9$. Theor-

etical calculations that fit optical data give $N(\epsilon_F) \sim 2.1$ electron/eV-atom (Mueller, Garland, Cohen and Benneman, 1971). Hence, the maximum charge transfer becomes (0.38×2.1) electron ~ 0.8 electron. Hence, the corner atom at C_1 has closer to eight localized d-electrons than the nine prescribed by the electronic configuration. On the other hand, the surface atom S and the "inside corner" atom C_2 still retain nine localized d-electrons, so their hole charge density $\rho(\underline{r})$ may be described by the corresponding contours (rows 1 and 4 respectively), shown for $\text{Cu}^{++}(3d^9)$ in Figure 7. For the outer corner atom C_1 , if there were no charge transfer, than its $\rho(\underline{r})$ is given by the degenerate configurations given in rows 2 and 3 of Figure 7 for $\text{Cu}^{++}(3d^9)$; if there were complete charge transfer, then $\rho(\underline{r})$ is described by that at C_1 of Figure 6 for $\text{Ni}^{++}(3d^8)$. The estimated charge transfer of 0.8 electrons out of the C_1 sites for $\text{Pt}^+(5d^9)$ implies that there will be a resonance back and forth between the charge density configurations for C_1 in Figures 6 and 7. In principle, such a resonant state would be more reactive than a state which has the definite charge density configuration described by that of atom type S in Figure 7.

The conjecture that there is perhaps a connection between bulk Fermi level density of states and the catalytic activity of transition-metals in the same series is not new. However, due to the complexity of the problem, there is, to our knowledge, no existing quantitative theory. The inclusion of step geometries make the theoretical problem even more formidable. It is fortuitous that the physical parameters

involved in this systematic study of transition-metals in stepped surfaces has allowed us to make several simplifying approximations and make this model calculation tractable. The results of our calculation can interpret correctly the different roles played by atomic steps in the catalytically active metal Pt and the inert Au. It is well known that the chemisorption of gases on metal surfaces follow certain empirical rules of ordering (Somorjai and Szalkowski, 1971). These rules are mostly governed by steric considerations. We believe our results as displayed in Tables 1-3 and Figures 2-7 can shed light on the kind of chemical bonding that may be favored at various geometries for different metals with different d-level occupations.

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FIGURE CAPTIONS

- Fig. 1: Step geometries chosen for (a) the fcc structure and (b) the bcc structure.
- Fig. 2: One electron charge density angular distribution for bcc $V^{++}(3d^3)$.
- Fig. 3: One electron charge density angular distribution for bcc $Cr^{++}(3d^4)$.
- Fig. 4: One hole charge density angular distribution for fcc $Fe^{++}(3d^6)$.
- Fig. 5: One hole charge density angular distribution for fcc $Co^{++}(3d^7)$.
- Fig. 6: One hole charge density angular distribution for fcc $Ni^{++}(3d^8)$.
- Fig. 7: One hole charge density angular distribution for fcc $Cu^{++}(3d^9)$.

TABLE 1Cubic Crystal Field Splitting Parameter $10Dq$ for the 3d Ions

Ions	V^{++}	Cr^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}
$10Dq$ (eV)	1.46	1.74	1.24	1.24	1.07	1.56

TABLE 2

Energies and Degeneracies of the Crystal Field Splittings
of the Free Ion Ground State in Different Surface Geometries

	${}^4F(V^{++})$	${}^5D(Cr^{++})$	${}^5D(Fe^{++})$	${}^4F(Co^{++})$	${}^3F(Ni^{++})$	${}^2D(Cu^{++})$
Bulk Atom	0. 10.Dq (3) 18.Dq (3)	0. (2) 10.Dq (3)	0. (3) 10.Dq (2)	0. (3) 8.Dq (3) 18.Dq	0. 10.Dq (3) 18.Dq (3)	0. (2) 10.Dq (3)
Surface Atom S	0. 1. Dq 4.8Dq 8.1Dq 8.7Dq 9.8Dq 13.6Dq	0. 3.2Dq 7.5Dq 22. Dq 25.9Dq	0. 20. Dq 49.6Dq (2) 65.2Dq	0. (2) 7.9Dq 22.9Dq 24.2Dq (2) 25. Dq	0. (2) 1.1Dq 3.0Dq 18. Dq 26.9Dq (2)	0. 17.2Dq (2) 54.4Dq 71. Dq
Corner Atom C_1	0. 5. Dq (3) 9. Dq (3)	0. (2) 5. Dq (3)	0. (3) 5. Dq (2)	0. (3) 4. Dq (3) 9. Dq	0. 5. Dq (3) 9. Dq (3)	0. (2) 5. Dq (3)
Corner Atom C_2	Same as for Bulk		0. 10.1Dq 52.7Dq 73.1Dq 89.8Dq	0. 0.6Dq 15.1Dq 20.9Dq 28.1Dq 34. Dq 38.5Dq	0. 4.2Dq 11.4Dq 18.3Dq 24.8Dq 40.4Dq 41. Dq	0. 18. Dq 38.2Dq 89.4Dq 97.7Dq

TABLE 3

Many Electron Ground States in Various Crystal Fields for the 3d Ions

Ion	Surface Atom S	Corner Atom C ₁	Corner Atom C ₂
V ⁺⁺ (3d ³)	.4736(33>+i 3-3>)- -.5251(3-1>+i 31>)	$\frac{1}{\sqrt{2}} (32>- 3-2>)$	Same as C ₁
Cr ⁺⁺ (3d ⁴)	.4117(22>- 2-2>)- -.8130 20>	$\frac{1}{\sqrt{2}} (22>+ 2-2>) \left\{ \begin{matrix} (2) \\ 20> \end{matrix} \right.$	Same as C ₁
Fe ⁺⁺ (3d ⁶)	.8455 22>-.5355 2-2>	$\frac{1}{\sqrt{2}} (22>- 2-2>) \left\{ \begin{matrix} (3) \\ 2 > \\ 2-1> \end{matrix} \right.$	.6385(2-2>- 22>)- -.3037(21>+ 2-1>)
Co ⁺⁺ (3d ⁷)	$\left. \begin{matrix} -.9689 33>-.2475 3-1> \\ -.2475 31>-.9689 3-3> \end{matrix} \right\} (2)$	$\left. \begin{matrix} .7906 33>+.6124 3-1> \\ -.6124 31>-.7906 3-3> \\ 30> \end{matrix} \right\} (3)$	.6492(3-3>- 33>)- -.266(32>+ 3-2>)+ +.0873(31>- 3-1>)+ +.0136 30>
Ni ⁺⁺ (3d ⁸)	30>	$\frac{1}{\sqrt{2}} (32>- 3-2>)$	-.0685(33>+ 3-3>)+ +.4782(32>- 3-2>)- -.5163(31>+ 3-1>)
Cu ⁺⁺ (3d ⁹)	20>	$\frac{1}{\sqrt{2}} (22>+ 2-2>) \left\{ \begin{matrix} (2) \\ 20> \end{matrix} \right.$	-.0662(22>+ 2-2>)+ +.4573(21>- 2-1>)- -.757 20>

00004407296

Atom Type S

Atom Types C_1 and C_2

Figure 2

Atom Type S

Atom Types C_1 and C_2 (2-fold Degenerate)

Figure 3

Atom Type S

Atom Type C_1 (3-fold Degenerate)

Atom Type C_2

Figure 4

Atom Type C_1 (3-Fold Degenerate)

Atom Type C_2

Figure 5

Atom Type S

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Atom Type C_1 Atom Type C_2

Figure 6

Atom Type S

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Atom Type C_1 (2-Fold Degenerate)

Atom Type C_2

Figure 7

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