

Effect of disorder on the electronic structure of palladium

S. K. Bose

*Department of Physics, Brock University, St. Catharines, Ontario, Canada L2S 3A1**
and Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65,
D-7000 Stuttgart 80, Federal Republic of Germany

J. Kudrnovsky,[†] I. I. Mazin,[‡] and O. K. Andersen

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65,
D-7000 Stuttgart 80, Federal Republic of Germany

(Received 18 December 1989)

We have studied the effect of disorder on the electronic structure of palladium using linear muffin-tin orbitals (LMTO) – recursion and LMTO–coherent-potential-approximation (CPA) techniques. Disorder is simulated by moving atoms, via the Metropolis Monte Carlo method, from their crystalline positions, as well as by putting in vacancies. The electronic density of states (DOS) is calculated for varying degrees of positional disorder and vacancy concentrations. The peaked structure of the DOS at the Fermi energy is found to survive large vacancy concentrations ($\sim 6\%$) as long as the fcc crystal structure is maintained or only weakly perturbed. Thus, some amount of positional disorder is essential in reducing the DOS at the Fermi level to the extent that the spin fluctuations can be suppressed to render the system superconducting. We argue, as well as present evidence to the effect, that while positional disorder can lower the DOS at the Fermi level and hence the tendency to magnetic ordering, the electron-phonon coupling remains nearly as strong as in pure crystalline palladium, thus explaining the observed superconductivity in irradiated films of palladium reported by Stritzker [Phys. Rev. Lett. **42**, 1769 (1979)].

I. INTRODUCTION

The unique electronic structure of palladium makes it one of the most interesting transition metals to study theoretically or experimentally. It has one of the highest electronic densities of states at the Fermi level, yet it is neither magnetic nor superconducting. It is believed that the large paramagnetic susceptibility and Stoner enhancement factor result in significant spin-fluctuation effects, preventing crystalline palladium from becoming superconducting. However, irradiated films (of thickness 200–1000 Å) of palladium have been found to become superconducting at and below a temperature, $T_c \cong 3$ K.¹ The standard explanation is that the sharp peak in the density of states at the Fermi energy, $N(E_F)$, is smeared out in the disordered phase. This reduces $N(E_F)$ and hence the Stoner factor. The spin fluctuations are then no longer strong enough to suppress a transition to the superconducting phase. However, Appel *et al.*² have argued that because of strong scattering in the presence of disorder, a significant reduction in the dynamical spin susceptibility, and hence spin fluctuations, can occur without a significant decrease in $N(E_F)$. It is usually expected that a decrease in $N(E_F)$ would lead to a decrease in the electron-phonon coupling (BCS phonon parameter λ) and thus be detrimental to superconductivity. From this standpoint the scenario in which the dynamical spin susceptibility or the effective Stoner factor can be lowered without a reduction in $N(E_F)$ is certainly attractive.

The conclusion of Appel *et al.*,² that it is not necessary to lower $N(E_F)$ in order to lower the dynamical spin sus-

ceptibility, is arrived at by using a configurational averaging procedure based on the random-phase model of amorphous solids.^{3–5} One can thus raise the question as to whether the kind of disorder (strong scattering limit) for which such an averaging procedure is valid can also leave $N(E_F)$ essentially unaffected. In particular one would like to know whether $N(E_F)$ in the presence of disorder, as induced by irradiation of Pd films that are found to be superconducting, deviates significantly from its crystalline value. This question can be answered properly only by reliable electronic structure calculation for models of Pd that incorporate sufficient disorder, as would be expected in particle-irradiated samples. In the present paper we address this particular issue and carry out the electronic structure calculation of Pd for various degrees of disorder. To this end we have adopted the first-principles linear muffin-tin orbitals (LMTO) scheme, combined with the recursion and the coherent-potential approximation (CPA) methods, and have tried to avoid the pitfalls commonly associated with (semi)empirical tight-binding methods.

Since detailed structural study of the irradiated samples of Pd which were found to be superconducting is not available, we cannot build models that would be faithful reproductions of these samples. Hence instead of attempting to simulate radiation damage in Pd, we introduce disorder in the crystal gradually and study the concurrent change in the electronic structure. We can quantify the disorder by specifying features such as vacancy concentration, pair-distribution function, root-mean-square displacement of the atoms, etc., and can ascertain

to what extent these should change in order to bring about a given change in $N(E_F)$. One can then speculate whether the type and amount of disorder necessary of this change in $N(E_F)$ can indeed be present in Pd samples irradiated with a 130-keV He^+ beam, as in the experiment of Stritzker.¹ According to Stritzker, during the irradiation at low temperatures, vacancies and Pd atoms located at interstitial sites (Frenkel pairs) are created in the sample, which are responsible for the superconducting behaviors of the latter. It is also speculated that not only Frenkel pairs are produced in these samples, but perhaps also agglomerations of interstitials and vacancies as a result of rather high local temperatures during the irradiation. Our attempt has been to study the change in the electronic structure by gradually increasing the disorder. Hence, to start with, we perform a series of calculations by putting in vacancies in increasing concentration in an otherwise perfect lattice. In the next step we perform calculations on model clusters of Pd in which atoms are moved from their ideal lattice positions. Finally, we study the effect of incorporating vacancies in such a disordered solid.

We have used LMTO-recursion⁶ and LMTO-CPA (Ref. 7) techniques to study the effect of disorder on the electronic structure of Pd. The recently developed LMTO-CPA method is used to study the effect of putting vacancies at random at a certain percentage of sites in a perfectly ordered lattice, i.e., vacancies appear as random substitutional impurities in an ordered lattice in these calculations. This is described in Sec. II of this paper. Section III describes the recursion-method calculations, where both the effects of positional disorder and vacancies are studied. In Sec. IV we present a discussion as to the strength of the electron-phonon coupling in such disordered models of Pd. In Sec. V we discuss the relevance of the present calculation in understanding the superconductivity in disordered (irradiated) samples of Pd, and present our conclusions.

II. EFFECT OF VACANCIES IN AN ORDERED LATTICE

To start with, we perform a set of standard LMTO calculations for the fcc lattice using 16- (tetragonal) and 32- (cubic) particle unit cells, where the origin is taken as a vacancy (a missing atom), while the rest of the sites in the unit cell are supposed to be occupied by Pd atoms. The calculations show the effect of vacancies, at the 6% and 3% concentration levels, on the electronic structure of palladium in a perfectly ordered lattice, where the vacancies themselves are repeated periodically in space. However, the main purpose of this preliminary set of calculations is to obtain self-consistent potential parameters for the vacancy and Pd atoms, which can be transferred to the calculation for the disordered phase. For the 16-particle tetragonal unit cell we have performed two sets of calculations. In one set of calculations we classify the atoms in the unit cell according to their point-group symmetry. With the origin of this unit cell considered as a vacancy, there are six inequivalent classes of Pd atoms in the cell. Thus we obtain six sets of potential parameters for these six classes of Pd atoms and the parameters for

the vacancy. For later application of these potential parameters in the LMTO-CPA and LMTO-recursion calculations we would like, in order to keep the calculations less time consuming, only one set of potential parameters for the Pd atoms and one for the vacancies. To test the reliability of such a scheme we repeat the calculation for the 16-particle unit cell by considering all the Pd atoms as equivalent. In this case the potential parameters for the Pd atom are calculated by considering the average of the potentials in all the Pd spheres in the unit cell. We find that the total density of states per atom obtained in these two sets of calculations are remarkably similar. Since we are primarily interested in this quantity only, we have decided to follow the scheme of using only one set of parameters for all the Pd atoms. Thus the 32-particle-unit-cell calculation is also performed by considering all the Pd atoms in the unit cell as equivalent.

All the above LMTO calculations are performed using the atomic-sphere approximation (ASA),⁸ where the space is divided into volume filling, and hence overlapping. Wigner-Seitz (WS) spheres centered at the lattice sites. Inside these spheres the charge density and potential are approximated by their spherical averages. Errors due to the ASA can be minimized by incorporating to so-called "combined correction" terms.⁸ We have included the combined correction following a method suggested in Ref. 9, based on the energy derivative of the screened (tight-binding) structure constant matrix. The Brillouin-zone integrations are performed with the tetrahedron method, using its latest version, which avoids misweighting and corrects errors due to the linear approximation of the bands inside each tetrahedron. The k points are chosen on an equispaced mesh. The LDA approximation of von Barth and Hedin¹⁰ is used.

The electronic density of states per atom obtained in the 16- and 32-particle-unit-cell calculations as well as that for pure palladium is shown in Fig. 1. In Table I we present the Fermi energy (E_F) and the density of states at the Fermi energy [$N(E_F)$] for the three cases. It is apparent that vacancies arranged periodically in a periodic lattice, up to a concentration of 6%, has an inappreciable effect on the electronic structure. As we increase the concentration of vacancies, the number of electrons per atom decreases, and the Fermi energy shifts to a lower value. Thus although the height of the peak (near E_F) in the DOS diminishes with increasing vacancy concentration, the actual value of $N(E_F)$ is affected to a lesser degree. It is possible that the peak in the DOS survives purely due to the underlying periodicity, which has not been perturbed. Also, since, the vacancies stay at fixed distances from each other, the effect of agglomeration of vacancies cannot show up in such calculations. Thus, in the next step of our investigations we study the effect of putting in vacancies at random in a periodic lattice, where they have a nonzero probability of coming close to each other. This calculation is done using the LMTO-CPA technique, where we use the potential parameters obtained in the standard LMTO calculation for pure Pd and the 16- and 32-particle unit cells containing one vacancy.

The LMTO-CPA method has been discussed in some recent publications.⁷ The starting point is the LMTO

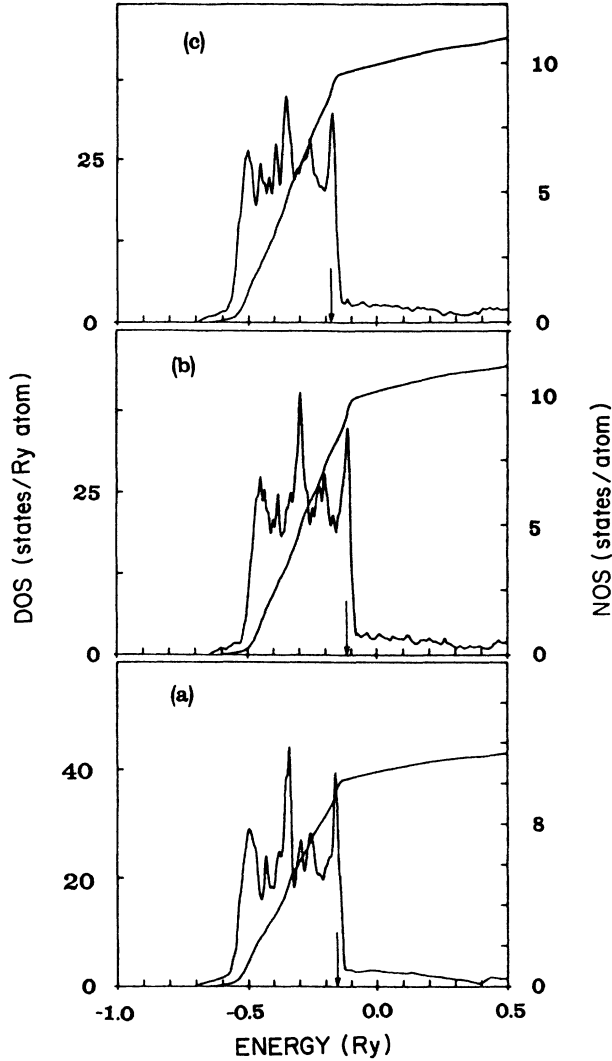


FIG. 1. DOS of crystalline (fcc) Pd with periodically arranged vacancies; (a) pure fcc crystal, (b) fcc crystal with $\frac{1}{32}$ vacancies, (c) fcc crystal with $\frac{1}{16}$ vacancies. The arrows indicate the positions of the Fermi levels E_F . E_F and $N(E_F)$ are given in Table I.

TABLE I. Fermi energy (E_F) and DOS at E_F , $N(E_F)$, from the standard LMTO calculation.

| System | E_F (Ry) | $N(E_F)$ (States/Ry atom) |
|---|---------------|------------------------------|
| fcc Pd | -0.1544 | 32.3 |
| fcc Pd with 3% vacancy (32-particle cell (cubic) with one missing atom) | -0.1211 | 29.0 |
| fcc Pd with 6% vacancy (16-particle cell (tetragonal) with one missing atom) | -0.1694 | 27.2 |

Hamiltonian in the nearly orthogonal representation γ :

$$H_{\mathbf{R}L,\mathbf{R}'L'}^\gamma = C_{\mathbf{R}L} \delta_{\mathbf{R}\mathbf{R}'} \delta_{LL'} + (\Delta_{\mathbf{R}L})^{1/2} \times [S^0(1-\gamma S^0)^{-1}]_{\mathbf{R}L,\mathbf{R}'L'} (\Delta_{\mathbf{R}'L'})^{1/2}. \quad (1)$$

Here \mathbf{R} denotes a lattice site and $L=(l,m)$ ($l \leq 2$) is a (collective) orbital index. The quantities $X=C,\Delta,\gamma$, called the potential parameters, are matrices diagonal with respect to indices \mathbf{R} and L , and $X_{\mathbf{R}L}(=X_{\mathbf{R}l})$ are independent of the index m . In general, the quantities $X_{\mathbf{R}L}$ describe the scattering properties of the atoms placed at the lattice site \mathbf{R} . In the LMTO-CPA calculation they take randomly the values for Pd and vacancy (determined by the vacancy concentration) with probabilities $(1-x)$ and x , where x is the vacancy concentration. The structure enters via nonrandom structure constant S^0 with elements $S_{\mathbf{R}L,\mathbf{R}'L'}^0$. The Hamiltonian (1) is treated within the coherent-potential method using the single-site approximation (SSA). The Green's function corresponding to the Hamiltonian (1) is transformed from the γ -LMTO representation to an auxiliary representation, where the CPA configurational averaging can be done exactly within the SSA. After performing the configurational averaging we revert back to the original physical LMTO representation γ . For further details readers should consult Ref. 7.

In Fig. 2 we show the results for the DOS per atom for pure Pd as well as for various concentrations of vacancies obtained by the LMTO-CPA method. In Table II we present the corresponding values of E_F and $N(E_F)$. The potential parameters for the 6% and 3% vacancy calculations are the same as those obtained in the standard self-consistent LMTO calculations for the 16- and 32-particle unit cells, respectively, while those used in the calculation for pure Pd are the ones obtained in the standard LMTO calculation for pure fcc Pd. In these LMTO-CPA calculations the lattice is supposed to be fcc, and hence the disorder is only in the position of the vacancies. Thus the calculation is in the spirit of a substitutionally disordered alloy. The calculation is carried out by assigning appropriate probabilities to various random configurations of vacancies in fcc palladium for a given concentration, and configurations with agglomerations of vacancies are attributed a small but nonzero probability. In the calculation for 9% vacancies we have used the potential parameters from the 16-particle-unit-cell (corresponding to 6% vacancies) standard LMTO calculation. However, the corresponding loss in accuracy in the calculated DOS is minimal in our opinion, insofar as one is interested in studying the change in the DOS only. In practice it is doubtful whether such a large concentration of vacancies is achieved even in irradiated samples. The important point is that even with such a large concentration of vacancies the change in the DOS at the Fermi energy is not large enough to suppress the spin fluctuations significantly if the lattice structure is unperturbed. The peak in the DOS near the Fermi energy is a characteristic of the fcc structure and survives any reasonably large concentration of vacancies as long as the lattice remains fcc. In the next section we study the effect of positional

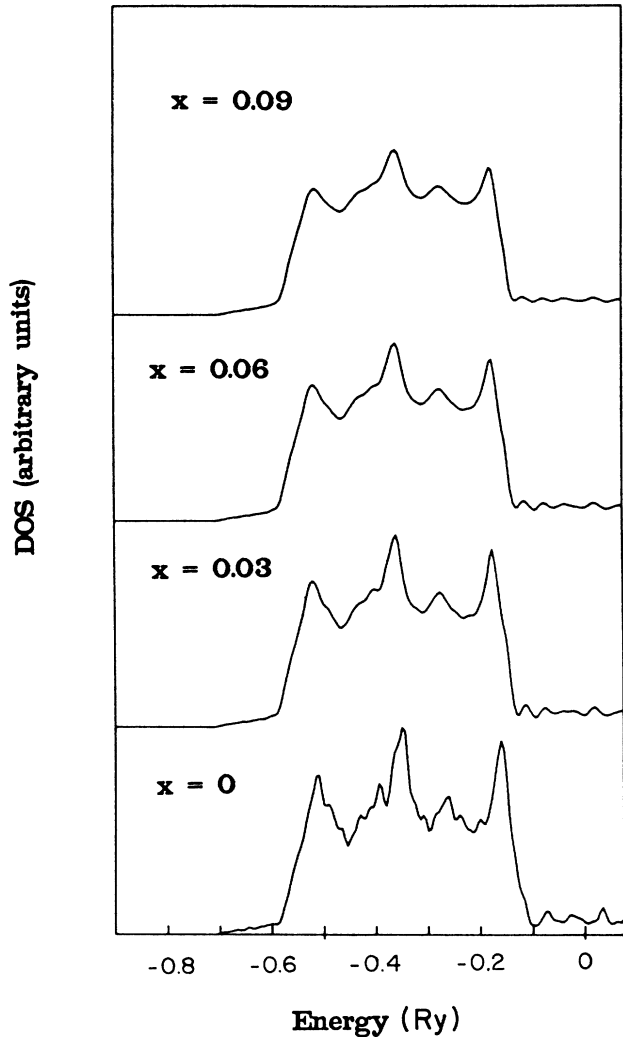


FIG. 2. DOS of crystalline (fcc) Pd with vacancies as random substitutional impurities calculated via the LMTO-CPA method. x is the vacancy concentration. See Table II for values of E_F and $N(E_F)$.

TABLE II. Fermi energy (E_F) and DOS at E_F , $N(E_F)$, from the LMTO-CPA calculation. Vacancies appear as random substitutional impurities in an fcc lattice.

| System | E_F (Ry) | $N(E_F)$ (States/Ry atom) |
|---------------------------|---------------|------------------------------|
| fcc Pd | -0.1405 | 29.4 |
| fcc Pd with 3% vacancy | -0.1555 | 28.6 |
| fcc Pd with 6% vacancy | -0.1578 | 26.9 |
| fcc Pd with 9% vacancy | -0.1604 | 25.3 |

disorder as well as vacancies on the electronic structure of Pd.

III. EFFECT OF POSITIONAL DISORDER AND VACANCIES

In order to study the effect of positional disorder on the electronic structure we construct 500-atom model clusters by using the Metropolis Monte Carlo scheme.¹¹ We use a pair potential of the Lennard-Jones for m whose parameters are fitted to the lattice parameter and the cohesive energy of fcc palladium.¹² The simulation is carried out at a temperature above the melting point of solid palladium. However, instead of carrying out the simulation to equilibrium, which would give a model for liquid palladium, we select some initial configurations. In particular we have performed the electronic-structure calculation for two such models, where the amount of disorder in one is greater than that of the other. We characterize the amount of disorder by the rms displacement of atoms and the pair-distribution function. The model with smaller disorder, with a smaller rms displacement of the atoms and sharper peaks in the pair-distribution function, will be referred to as model 1. The model with larger disorder will be referred to as model 2. The rms displacement of atoms in models 1 and 2 are, respectively, 4.25% and 6.21% of the nearest-neighbor separation, and their pair-distribution functions, along with that for an fcc cluster, are shown in Fig. 3. Stritzker¹ estimates the lattice constant of the irradiated superconducting samples of Pd to be 0.4% larger than in the normal state. However, the effect of such a small change in the lattice parameter on the electronic structure will be small. Thus the number density of the clusters, without the vacancies, is chosen as that of fcc palladium. The potential parameters, as calculated by using the standard LMTO method, are for the lattice constant appropriate for the normal-state fcc palladium.

The electronic structure of these clusters can be studied by applying the recursion method to the tight-binding (TB) LMTO Hamiltonian $\bar{H}^{(1)}$:

$$\bar{H}^{(1)} = \bar{C} + \bar{\Delta}^{1/2} \bar{S} \bar{\Delta}^{1/2}, \quad (2)$$

where the TB potential parameters \bar{C} and $\bar{\Delta}$ and the TB structure constants $\bar{S}_{RL,R'L'}$ are to be obtained from the corresponding standard LMTO quantities by following the prescription of Refs. 8 and 9. One can also consider the more accurate γ -LMTO Hamiltonian (1), related to $\bar{H}^{(1)}$ via the infinite series:

$$H^\gamma = H^{(2)} = \bar{H}^{(1)} - \bar{h} \bar{o} \bar{h} + \bar{h} \bar{o} \bar{h} \bar{o} \bar{h} - \dots, \\ \bar{h} = \bar{H}^{(1)} - E_v. \quad (3)$$

where the parameter \bar{o} can be obtained from the standard LMTO parameters. This Hamiltonian is not tight binding, i.e., its matrix elements are not short ranged. The matrix elements of $\bar{H}^{(1)}$ or $\bar{S}_{RL,R'L'}$ essentially vanish beyond the second nearest neighbor, but the successive terms in the series expansion (3) connect orbitals centered on further and further sites. To improve upon the accuracy obtained by using only $\bar{H}^{(1)}$, while still having the

benefit of a tight-binding Hamiltonian appropriate for a real-space calculation, we consider the correction to $\bar{H}^{(1)}$ due to the addition of the term $\bar{h} \bar{o} \bar{h}$. This term should connect orbitals further away than the second nearest neighbors. However, we consider only the nonzero terms of $\bar{H}^{(1)}$ and update them due to the inclusion of the correction term $\bar{h} \bar{o} \bar{h}$. Orbitals that are unconnected via $\bar{H}^{(1)}$ are still left unconnected. This way the most significant part of the correction $\bar{h} \bar{o} \bar{h}$ is included in the calculation without increasing the size of the matrices involved. For details readers should consult Ref. 6(b).

In Fig. 4(a) and 4(b) we show the DOS calculated for a 500-atom fcc cluster by applying the recursion method to $\bar{H}^{(1)}$ and the approximate form of $H^{(2)}$ [the truncated form of series (3)] with periodic boundary conditions.

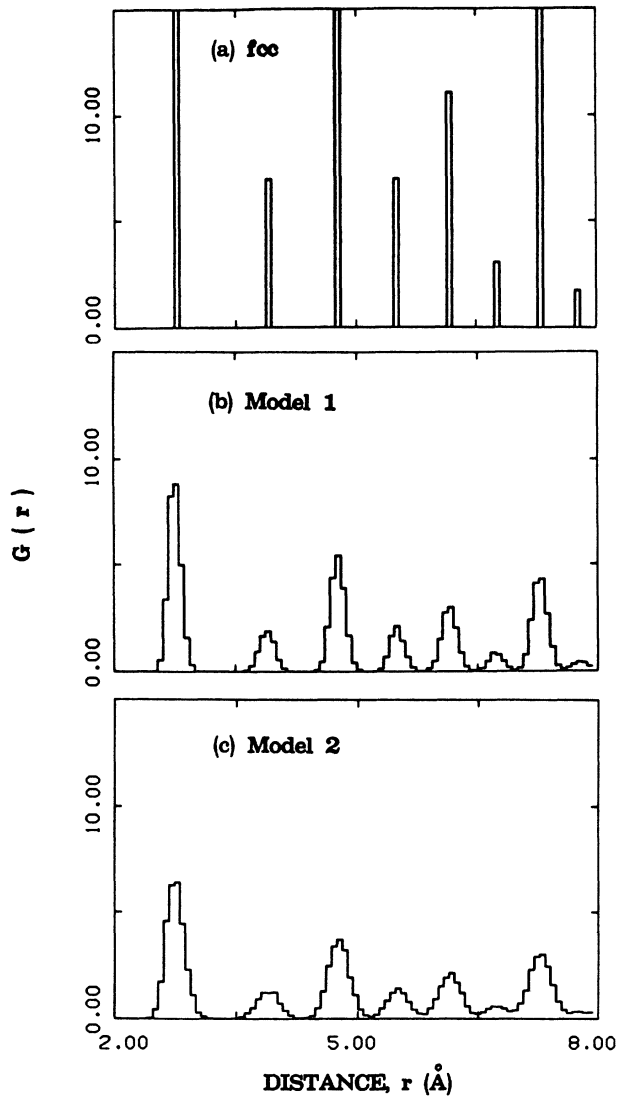


FIG. 3. Pair-distribution functions $G(r)$: (a) fcc Pd, (b) 500-atom cluster with rms displacement of atoms equal to 4% of the nearest-neighbor separation (disordered model 1), (c) 500-atom cluster with rms displacement of atoms equal to 6% of the nearest-neighbor separation (disordered model 2).

For comparison, in the window (c) of Fig. 4 we show the DOS obtained for fcc Pd obtained via the conventional Brillouin-zone summation (linear tetrahedron) method applied to the Hamiltonian $H^\gamma = H^{(2)}$ in its exact form. Here the ‘‘combined correction’’ terms are not included. The difference in Figs. 4(b) and 4(c) gives us an idea as to the errors involved in the recursion method, due to finite cluster size and the termination of the continued fraction, as well as due to the neglect of the higher-order terms in $\bar{H}^{(1)}$. The recursion-method calculations are performed

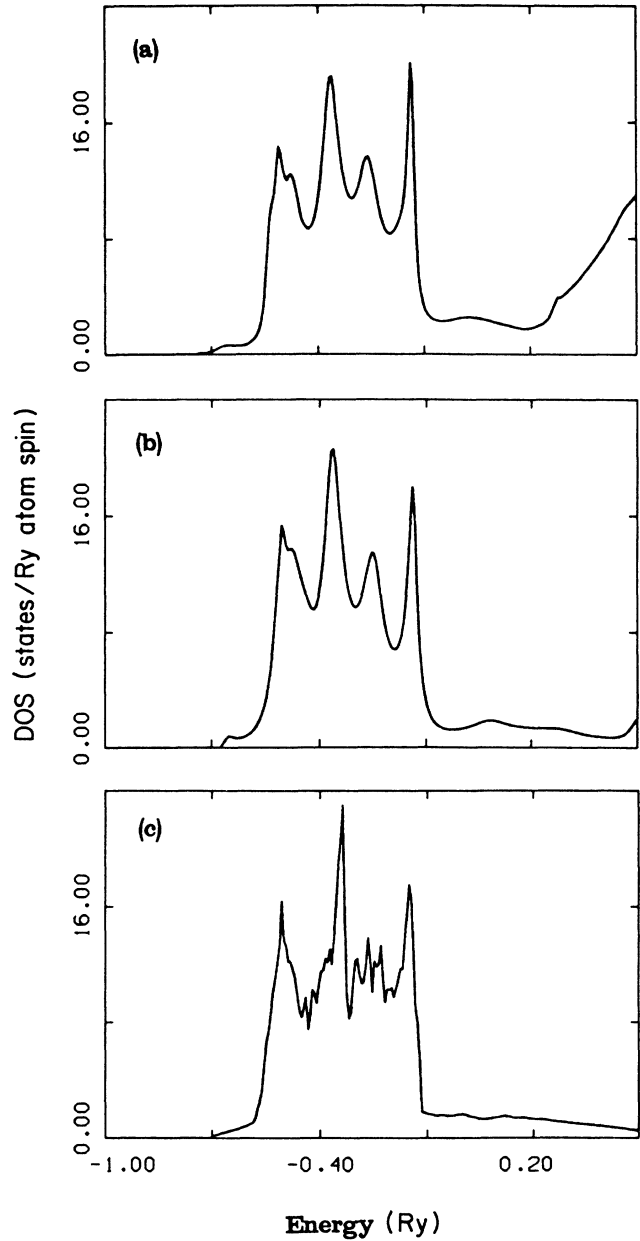


FIG. 4. (a) DOS of fcc Pd calculated by applying recursion method to the TB Hamiltonian $\bar{H}^{(1)}$ for a 500-atom cluster, (b) DOS for the same cluster obtained by applying recursion method to the Hamiltonian $\bar{H}^{(1)} - \bar{h} \bar{o} \bar{h}$, (c) DOS for fcc Pd obtained by using the Hamiltonian H^γ and the Brillouin-zone summation (linear tetrahedron) method.

using the termination scheme of Allan,¹³ which is capable of reproducing the sharp features of the DOS to a considerable extent. It is apparent from Figs. 4(a) and 4(b) that only for states of considerably higher energy than the Fermi level, the two Hamiltonians, $\bar{H}^{(1)}$ and $H^{(2)}$, yield significantly different results. However, since the calculation involving the approximate form of $H^{(2)}$ demands only a moderately larger computation time in comparison with $\bar{H}^{(1)}$, we have performed all the recursion calculations using the former form.

Figure 5 displays the DOS per atom for the two disordered models as well as that for an fcc cluster for comparison, all obtained with the Hamiltonian $H^{(2)}$ in its

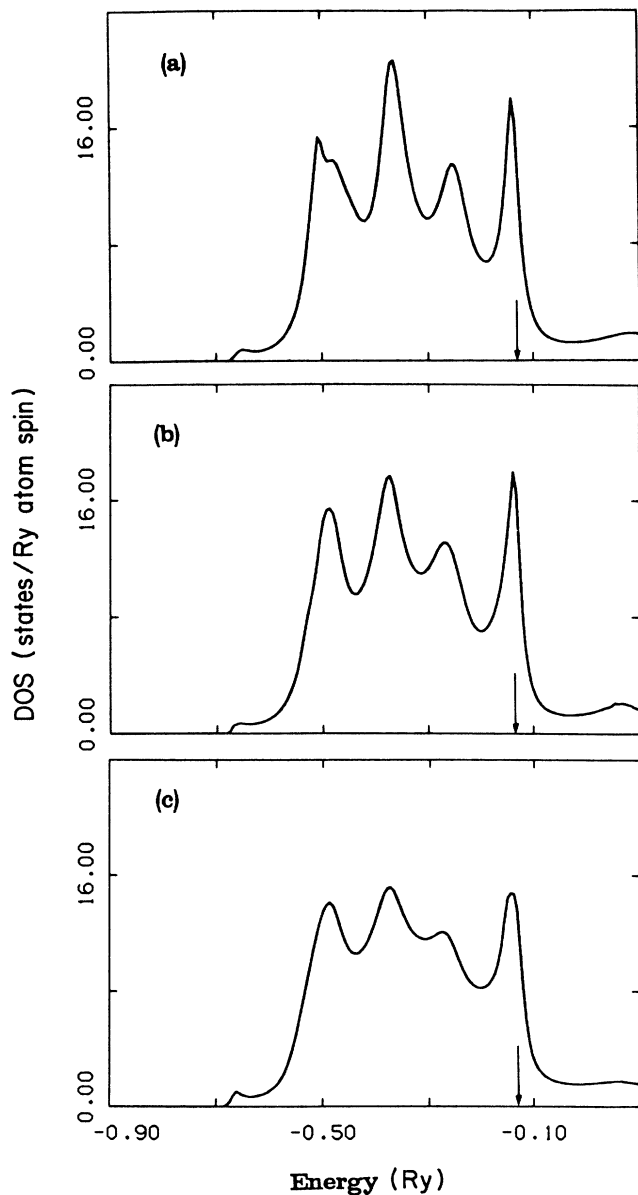


FIG. 5. DOS of Pd obtained via the recursion method applied to the Hamiltonian $\bar{H}^{(1)} - \bar{h} \bar{\sigma} \bar{h}$ for 500-atom clusters; (a) fcc, (b) disordered model 1, (c) disordered model 2. Arrows indicate the positions of the Fermi levels.

truncated form. The potential parameters for these three DOS are the same as in pure fcc Pd. Thus the difference is only due to the difference in the structure constants. It is known that the potential parameters are atomiclike quantities. Without a change in the chemical nature of the atoms or in their number density, the potential parameters are expected to undergo only a small change, and the principal change in the electronic structure should arise from the change in the spatial arrangement of atoms. Thus the densities of states shown in Fig. 5 for the disordered models of Pd are only marginally less accurate than a fully self-consistent calculation might yield. The ratio of $N(E_F)$ for the disordered model 1 to that of fcc Pd is 0.96, while this number is 0.8 for the disordered model 2. These numbers reflect the importance of posi-

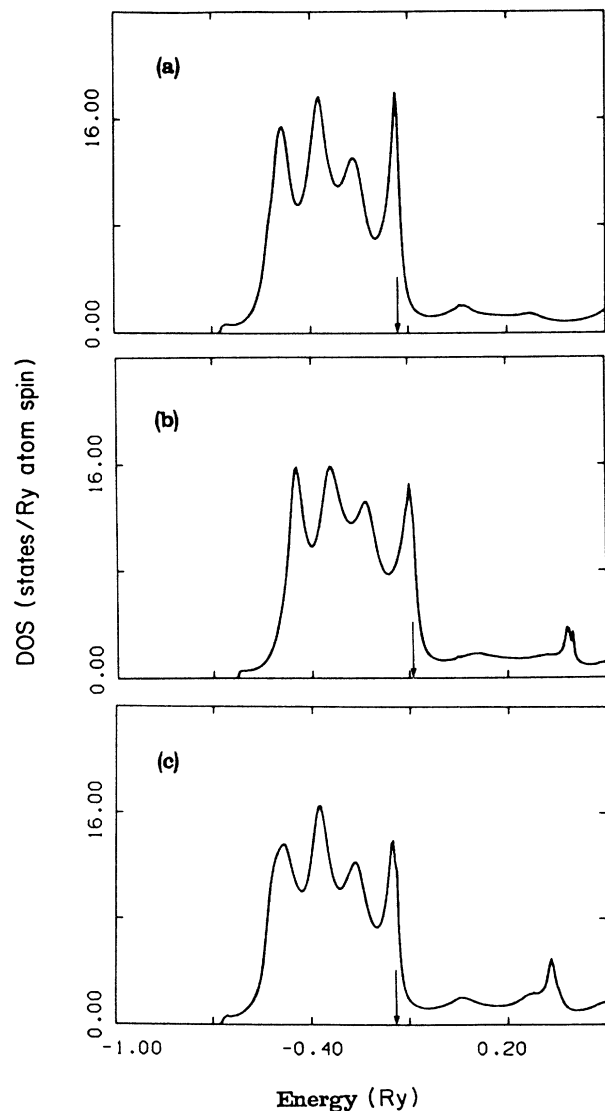


FIG. 6. Effect of vacancies on the DOS of the disordered model 1: (a) no vacancies, (b) 3% vacancies, (c) 6% vacancies. Arrows indicate the positions of the Fermi levels. See Table III for $N(E_F)$.

TABLE III. DOS at E_F , $N(E_F)$, in states/Ry atom for the positionally disordered models of Pd with and without vacancies, obtained via recursion method.

| Model 1 | | |
|--------------|--------------|--------------|
| No vacancies | 3% vacancies | 6% vacancies |
| 31.0 | 26.0 | 24.4 |
| Model 2 | | |
| No vacancies | 6% vacancies | 9% vacancies |
| 25.6 | 22.5 | 20.4 |

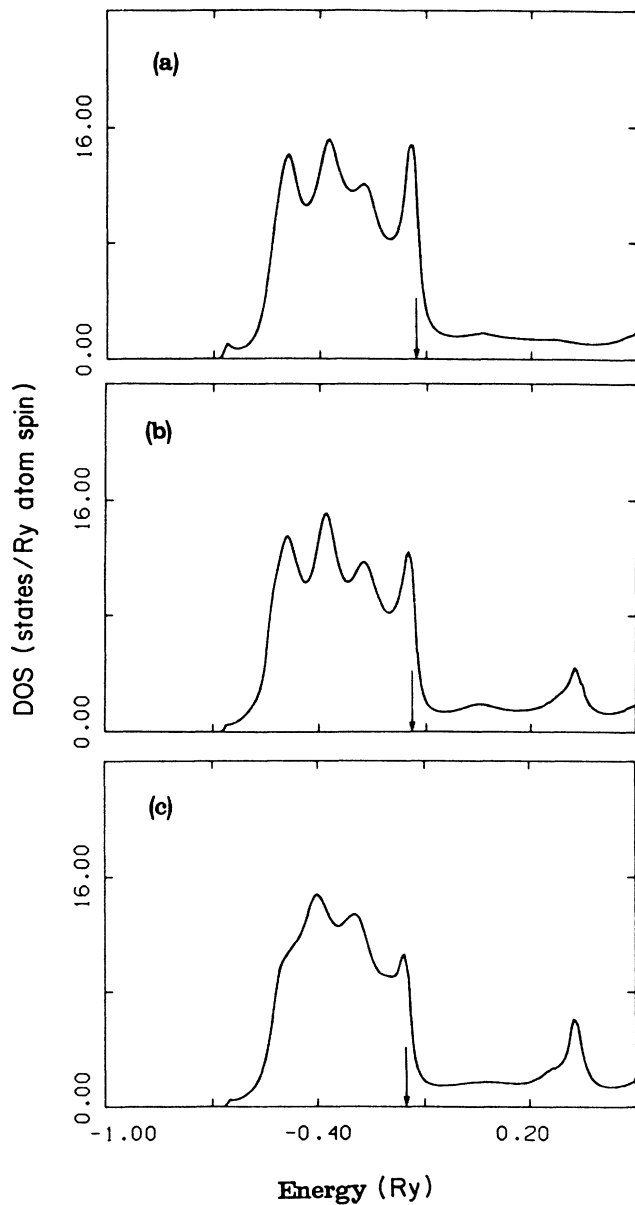


FIG. 7. Effect of vacancies on the DOS of the disordered model 2: (a) no vacancies, (b) 6% vacancies, (c) 9% vacancies. Arrows indicate the positions of the Fermi levels. See Table III for $N(E_F)$.

tional disorder in reducing the value of $N(E_F)$. For model 1, with an rms displacement of atoms equal to 4.25% of the nearest-neighbor separation, $N(E_F)$ decreases only to 15.5 states/Ry atom spin from a value of 16 states/Ry atom spin corresponding to the fcc phase. However, for a modest increase in disorder, as in model 2 with an rms displacement of atoms equal to 6.21% of the nearest-neighbor separation, this number is already down to 12.8 states/Ry atom spin.

Figures 6 and 7 display the effect of vacancies in the disordered models at various levels of concentration. Figures 6(a), 6(b), and 6(c) show the DOS for the disordered model 1, and the same model with 3% and 6% vacancies, respectively, the corresponding values of $N(E_F)$ being 15.5, 13.0, and 12.2 states/Ry atom spin. Figures 7(a), 7(b), and 7(c) show the DOS for the disordered model 2, and the same model with 6% and 9% vacancies, respectively. The corresponding values of $N(E_F)$ are 12.8, 11.5, and 10.2 states/Ry atom spin. The calculations for the 6% and the 9% vacancies concentrations were carried out with the same set of potential parameters, which were obtained with the standard LMTO calculation using the 16-particle unit cell described in the previous section. The peak around 0.2 Ry, far above the main Pd band, is the vacancy DOS whose strength grows with the vacancy concentration. The vacancy and Pd projected DOS's corresponding to Figs. 6(c) and 7(b), i.e., for 6% vacancy in models 1 and 2, respectively, are shown in Figs. 8(a) and 8(b).

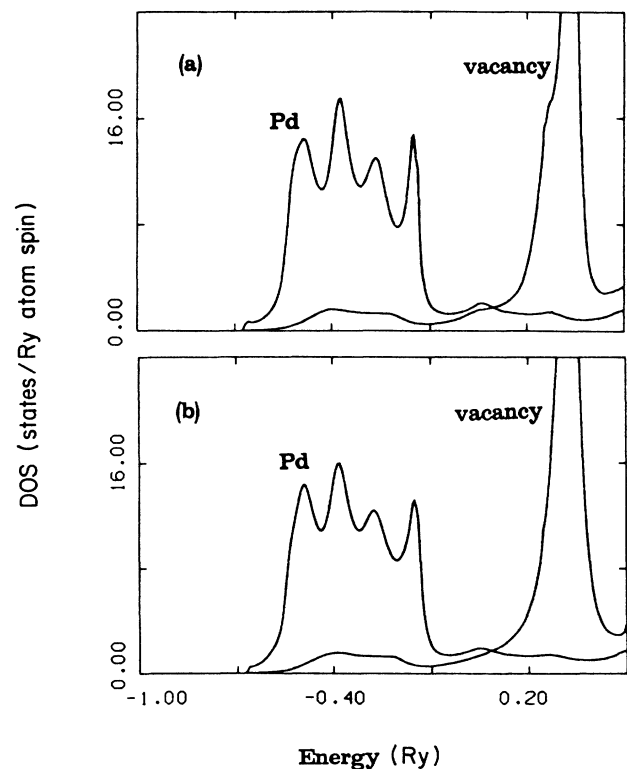


FIG. 8. Vacancy and Pd atom projected DOS for a 6% vacancy concentration: (a) disordered model 1, (b) disordered model 2.

The calculations presented in this section illustrate the importance of positional disorder in reducing the DOS at the Fermi level. We find that small deviation from the fcc structure does not cause any noticeable change in $N(E_F)$ or in the shape of the DOS curve. However, as the amount of disorder is increased, both $N(E_F)$ and the shape of the DOS are affected significantly. Vacancies in the disordered phase can introduce further decrease in the value of $N(E_F)$. Significant departure from the fcc structure is a prerequisite for reducing the peak in the DOS near the Fermi level.

IV. ELECTRON-PHONON COUPLING

In this section we present arguments as to how disorder may affect the electron-phonon coupling in Pd. First-principles calculations based on the rigid-muffin-tin approximation¹⁴ yield reasonably large values [0.2–0.6 (Refs. 15–19)] for the electron-phonon-coupling parameter λ in crystalline Pd. There are strong arguments that the above calculations for Pd are reliable. For instance, the phonon-limited resistivity, calculated in Ref. 18 in the same framework as used in the calculation of λ agrees rather well with the experiment. Also, the specific-heat enhancement suggests a reasonably large λ . A reasonable T_c is expected with such a large λ . The common opinion²⁰ as to the nonexistence of superconductivity in crystalline Pd is that it is nearly magnetic, and its tendency to superconductivity is suppressed due to strong electron-paramagnon scattering. Indeed, the paramagnetic susceptibility of crystalline Pd is quite large, and the calculated Stoner enhancement factor $S = [1 - N(E_F)I]^{-1}$ is greater than 5.^{21,22} The large values of the electron-phonon-coupling parameter λ and the Stoner factor S are both due to the large value of $N(E_F)$. It is thus reasonable to assume that any attempt to reduce the Stoner factor by reducing $N(E_F)$ will also lead to a decrease in λ , and the system might not exhibit superconductivity. In the following we argue that a decrease in $N(E_F)$ and hence the Stoner factor does not imply a proportional decrease in λ for a metal like Pd. In fact, our calculations suggest that for Pd it is quite possible to reduce $N(E_F)$ without affecting λ appreciably. The argument we produce is based on the result derived within the framework of the rigid muffin-tin approximation.

To gain some insight into the problem we have to separate out the nonatomiclike environment-dependent quantities such as $N(E_F)$ from atomiclike quantities associated with the Pd atom, which can be considered as transferable from one system to another in the first approximation. If there is no doping by other transition metals, it is a reasonable approximation to neglect all contributions to the Stoner factor S except for that from the d electrons of Pd. Then

$$S = [1 - N_{\text{Pd},d}(E_F)I_{\text{Pd},d}]^{-1}, \quad (4)$$

where $N_{\text{Pd},d}$ is the partial density of Pd d states. $I_{\text{Pd},d}$, being dependent on the solution of the radial Schrödinger equation inside the sphere at a Pd site [see Eq. (2.15) of

Ref. 21], can be considered to be an atomiclike quantity. When a perturbation is introduced into the system, such as doping or disordering, then $I_{\text{Pd},d}$ may be supposed to stay more or less unchanged, while $N_{\text{Pd},d}(E_F)$ should change. Thus, for palladium, for which more than 90% of the contribution to $N(E_F)$ comes from the d states, the change in the Stoner factor S should be dictated by the change in $N_{\text{Pd},d}(E_F)$.

The electron-phonon coupling with some approximation (see Ref. 23) may be written as

$$\lambda = \sum_i c_i \eta_i / (M_i \langle \omega^2 \rangle_i) \quad (5)$$

where c_i , M_i , and $\langle \omega^2 \rangle_i$ are the concentration, the mass, and the mean-square phonon frequency for the atom of the i th type. The electronic factor η_i for the atom of the i th type, in the so-called rigid muffin-tin approximation¹⁴ (see also Ref. 23), is given by

$$\eta_i = \sum_l \frac{(2l+2)}{(2l+1)(2l+3)} (V_{i,l+1}^i)^2 \times \frac{N_{i,l}(E_F)N_{i,l+1}(E_F)}{N(E_F)}, \quad (6)$$

where the matrix element of the electron-ion interaction, $V_{i,l+1}^i$, is some atomiclike quantity. For disordered Pd with vacancies only the Pd atoms contribute in (5). It is well known^{17,18,24} that for transition metals and in particular for Pd the dominating contribution in (5) is due to the d - f term, i.e.,

$$\eta_{\text{Pd}} \approx \frac{6}{35} (V_{d,f}^{\text{Pd}})^2 \frac{N_{\text{Pd},d}(E_F)N_{\text{Pd},f}(E_F)}{N(E_F)}, \quad (7)$$

or taking into account that

$$N(E_F) = \sum_{i,l} c_i N_{il}(E_F) \approx c_{\text{Pd}} N_{\text{Pd},d}(E_F),$$

$$\lambda \approx \frac{6}{35} \frac{N_{\text{Pd},f}(E_F)(V_{d,f}^{\text{Pd}})^2}{M_{\text{Pd}} \langle \omega^2 \rangle_{\text{Pd}}}. \quad (8)$$

Here we consider the fact that the density of states of Pd at the Fermi level is 97% of d character. So we come to the important conclusion that in the first approximation S follows the changes in $N_{\text{Pd},d}(E_F)$, while λ follows those in $N_{\text{Pd},f}(E_F)$.

In order to consider the variations in S and λ let us look at the total [Fig. 1(a)] and partial [Fig. 9(a)] DOS in fcc Pd. The large DOS (~ 30 states/Ry atom) at E_F is due to the peak in partial d DOS with a maximum just below the Fermi level. One way to reduce $N(E_F)$ is to shift the Fermi level up by doping, best of all by Ag, which is palladium's right neighbor. This was suggested by Gyoryffy *et al.*²⁵ It can be seen from Fig. 9 that as long as the fcc structure is retained the f DOS, $N_f(E_F)$ also decreases with the upward shift of the Fermi level, so not only S but also λ decreases. That is why Pd-Ag alloys are not superconducting, being nevertheless less magnetic than pure Pd.

An alternative way to reduce $N(E_F)$ is to smear out the peak near the Fermi level by strong disorder. We

have seen in Sec. III that this is possible only at the cost of a significant departure from the fcc structure. The smearing of the peak in $N_d(E_F)$ will certainly reduce S . To see the effect of such a disorder on λ , we have to ascertain how the f DOS changes as a result of disorder. It has not been possible for us to include the f orbitals in the basis for the recursion-method calculations involving large (500 particles) disordered models, simply because this would enormously increase the size of the matrices to be stored. Also, with the errors involved in the recursion method, a calculation of $N_f(E)$ which is ~ 100 times

smaller than $N_d(E)$ will not be reliable to the extent that one can correctly ascertain the effect of disorder on this particular quantity. Hence we have decided to estimate this effect indirectly. Using the standard LMTO method with an s, p, d, f basis we can calculate all the partial DOS's accurately for Pd for various crystalline structures, and study the simultaneous variations in $N_d(E_F)$ and $N_f(E_F)$. In Fig. 9 we compare $N_d(E)$ and $N_f(E)$ (magnified 75 times) for the fcc and the bcc structures. For a given structure the f DOS follows the general shape of the d DOS as a function of energy. This is to be

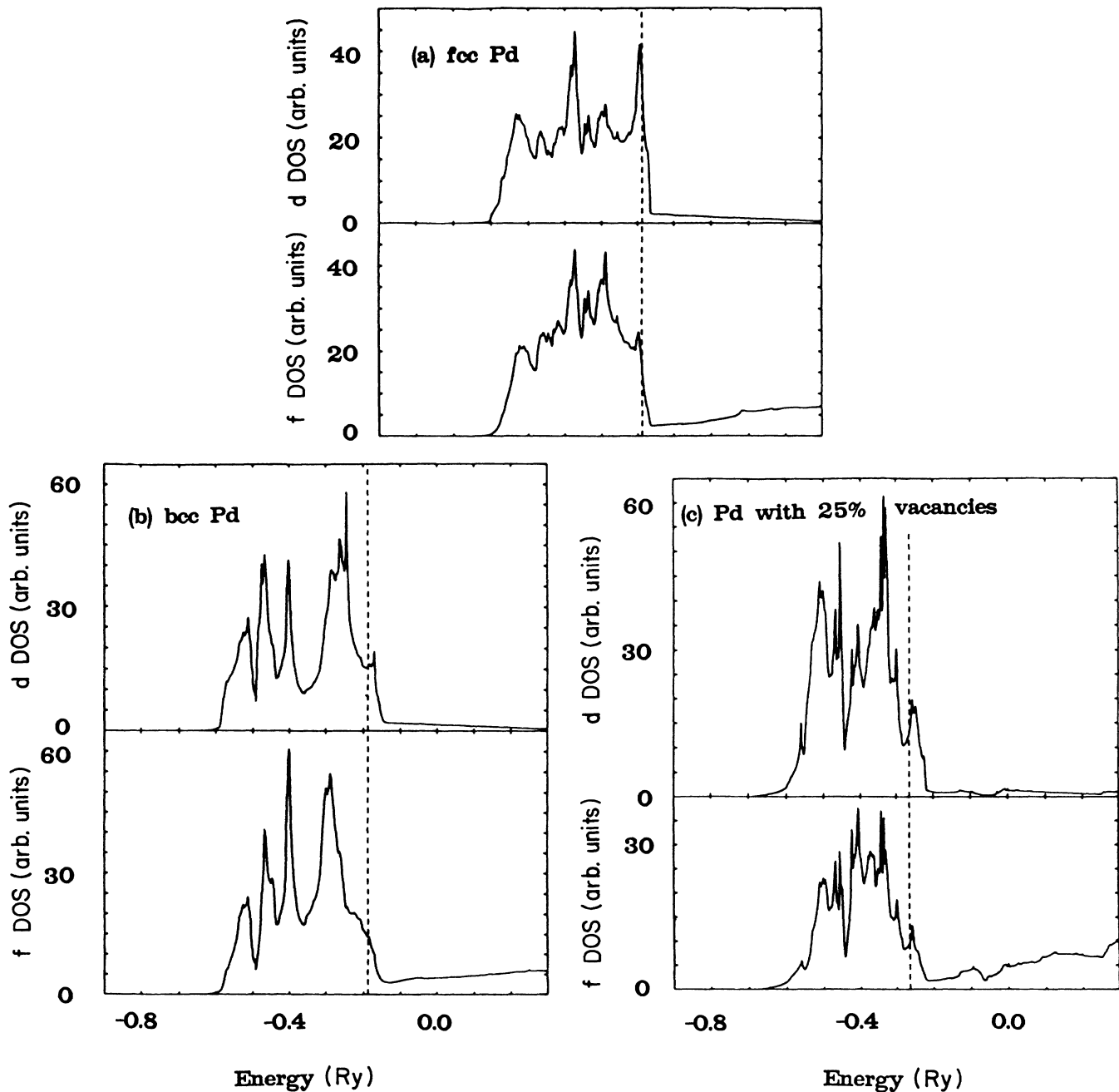


FIG. 9. Partial d - and f -state DOS for Pd atoms in (a) fcc Pd, (b) bcc Pd, (c) fcc Pd with 25% vacancies; upper panel— d DOS; lower panel— f DOS (magnified 75 times). Vertical dashed line indicates the position of the Fermi level.

expected, since the f character of the eigenstates arises from the d tails reaching an atom from its neighboring sites. However, the change in the f DOS at the particular energy, E_F , is not proportional to that in $N_d(E_F)$. The ratio of $N_f(E_F)/N_d(E_F)$ for the fcc structure is 0.0068, while for the bcc structure it is 0.0123. In Fig. 9(c) we show the partial d and f DOS projected on to the Pd atom for fcc Pd with 25% vacancies (one vacancy in a four-atom unit cell). Due to the large concentration of vacancies, the d -DOS for Pd changes from a value of 30 states/Ry atom for the pure system to 12.5 states/Ry atom (a factor of 2.4), while the f DOS decreases only by a factor of 1.6. The calculation for hcp Pd, not shown here, yield the values of $N_d(E_F)$ and $N_f(E_F)$ as 36.5 and 0.24 states/Ry atom, respectively. We also attempted to study the change in $N_d(E_F)$ and $N_f(E_F)$ by introducing disorder in four-particle unit cells of fcc Pd. We found that because of the small size of the unit cell the departure of these quantities from the corresponding fcc values were not significant. In our opinion, Figs. 9(a), 9(b), and 9(c) represent cases with drastic changes in the d DOS due to structural change and vacancy concentration, respectively, and we find that even for such drastic changes in the d DOS the corresponding change in the f DOS is rather small. The sensitivity of $N_d(E_F)$ to the atomic arrangement is due to the existence of the fcc-induced peak near E_F , and changing this arrangement either by switching to another crystal structure (bcc) or by disordering removes this peak. The f DOS, which has no such peak, does not show such an anomalous sensitivity to the atomic arrangement. Thus disorder affects the d DOS to a far greater extent than the f DOS. Unlike doping by Ag, positional disorder (and vacancies) is therefore the likely condition to reduce the Stoner factor S without substantially affecting the electron-phonon coupling.

We note that it is not necessary for the d - f term to be the most dominating one in (6) in order that the above arguments may hold. If we suppose that the p - d term is equally important, then we need to show that the p partial DOS is affected to a much lesser degree by disorder than the d DOS. Although we do not show the p DOS explicitly in Fig. 9, this is indeed supported by the calculations discussed in the previous paragraph.

V. SUMMARY OF RESULTS AND CONCLUSIONS

We have calculated the electronic structure of palladium as a function of positional disorder and vacancy concentration. We find that the peak in the DOS near the Fermi level, responsible for the high value of $N(E_F)$ in

Pd, can survive large vacancy concentration as long as the fcc structure is retained or only weakly perturbed. Significant departure from the fcc structure, combined with vacancy concentration of the order of 6%, can lower the value of $N(E_F)$ by 30% or more. This reduction in $N(E_F)$, which is mostly due to the reduction in the value of the d partial DOS can reduce the Stoner factor so that the spin fluctuations are suppressed substantially. We have argued and presented evidence, at least qualitatively, as to why the reduction in $N_d(E_F)$, and hence the Stoner factor, is not accompanied by a decrease in the electron-phonon coupling parameter λ , which is proportional to the f DOS, $N_f(E_F)$. This, in our opinion, describes the qualitative physics as to why irradiated thin films of Pd were found superconducting below 3 K by Stritzker.¹ The arguments presented by us also show why an attempt to achieve a superconducting system by doping Pd with Ag, where the fcc crystal structure is preserved, should fail. In this case both the d and the f partial DOS's are reduced simultaneously, i.e., a reduction in spin fluctuations is accompanied by a reduction in the electron-phonon coupling strength.

Appel *et al.*² have argued that the effective Stoner factor in the presence of strong disorder can be reduced without appreciably changing $N(E_F)$, and hence the electron-phonon coupling. This they proposed as an explanation of superconductivity in disordered Pd. Our calculations and arguments modify this picture somewhat without contradicting their main result. We believe that disorder as strong as considered in the work of Appel *et al.* should also change $N(E_F)$, causing a reduction in the Stoner factor in addition to what has been already estimated by these authors. This, we argue, does not imply a reduction in the electron-phonon coupling. One can thus combine the conventional wisdom about the appearance of superconductivity in disordered Pd with the picture proposed by Appel *et al.* These conclusions are substantiated by the experimental observation of a drastic reduction in the paramagnetic susceptibility of irradiated Pd samples by Meyer and Stritzker.²⁶

ACKNOWLEDGMENTS

One of us (S.K.B.) would like to acknowledge partial financial support by the Natural Sciences and Engineering Research Council (NSERC) of Canada. S.K.B. and J.K. acknowledge the warm hospitality of the members of the Max-Planck-Institut für Festkörperforschung, where most of this work was carried out. I.I.M. would like to thank the Alexander von Humboldt-Stiftung for financial support.

*Address for correspondence.

[†]Permanent address: Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, CZ-180 40 Prague 8, Czechoslovakia.

[‡]Permanent address: P.N. Lebedev Physical Institute of the Academy of Sciences of the U.S.S.R., Lenin Prospect 53, 117 924 Moscow, U.S.S.R.

¹B. Stritzker, Phys. Rev. Lett. **42**, 1769 (1979).

²J. Appel, D. Fay, and P. Hertel, Phys. Rev. B **31**, 2759 (1985).

³N. F. Mott, Philos. Mag. B **43**, 941 (1981).

⁴N. K. Hindley, J. Non-Cryst. Solids **5**, 17 (1970).

⁵L. Friedman, Philos. Mag. B **41**, 347 (1980); J. Non-Cryst. Solids **6**, 329 (1971).

⁶(a) S. K. Bose, K. Winer, and O. K. Andersen, Phys. Rev. B **37**, 6262 (1988); (b) S. K. Bose, S. S. Jaswal, O. K. Andersen, and J. Hafner, Phys. Rev. B **37**, 9955 (1988).

- ⁷J. Kudrnovsky, V. Drchal, and J. Masek, *Phys. Rev. B* **35**, 2487 (1987); J. Kudrnovsky and V. Drchal, *Solid State Commun.* **70**, 577 (1989).
- ⁸O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975); O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p. 59.
- ⁹O. K. Andersen, O. Jepsen, and M. Sob, in *Electronic Band Structure and Its Applications*, Vol. 283 of *Lecture Notes in Physics*, edited by M. Yussouff (Springer, Berlin, 1987), p. 1.
- ¹⁰U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- ¹¹N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
- ¹²K. Gschneidner, Jr., *Solid State Phys.* **16**, 275 (1964); C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 74.
- ¹³G. Allan, *J. Phys. C* **17**, 3945 (1984); in *The Recursion Method and its Applications*, Vol. 58 of *Springer Series in Solid State Sciences*, edited by D. G. Pettifor and D. L. Wearie (Springer-Verlag, Berlin, 1985).
- ¹⁴G. D. Gaspari and B. L. Gyorffy, *Phys. Rev. Lett.* **28**, 801 (1972).
- ¹⁵R. Evans, G. D. Gaspari, and B. L. Gyorffy, *J. Phys. F* **3**, 39 (1973).
- ¹⁶D. A. Papaconstantopoulos, L. L. Boyer, B. M. Klein, A. R. Williams, V. L. Moruzzi, and J. F. Janak, *Phys. Rev. B* **15**, 4221 (1977).
- ¹⁷W. H. Butler, *Phys. Rev. B* **15**, 5267 (1977).
- ¹⁸I. I. Mazin, E. M. Savitskii, and Yu. A. Uspenskii, *J. Phys. F* **14**, 167 (1984).
- ¹⁹F. J. Pinski, P. B. Allen, and W. H. Butler, *Phys. Rev. Lett.* **6**, 431 (1978); F. J. Pinski and W. H. Butler, *Phys. Rev. B* **19**, 6010 (1979).
- ²⁰G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2, p. 665.
- ²¹O. Gunnarsson, *J. Phys. F* **6**, 587 (1976).
- ²²J. F. Janak, *Phys. Rev. B* **16**, 255 (1977).
- ²³D. Rainer, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1986).
- ²⁴D. G. Pettifor, *J. Phys. F* **7**, 1009 (1977).
- ²⁵B. L. Gyorffy, A. Pindor, and W. M. Temmerman, *Phys. Rev. Lett.* **43**, 1343 (1979).
- ²⁶J. D. Meyer and B. Stritzker, *Phys. Rev. Lett.* **48**, 502 (1982).