number has no factor such as $T^{-3/2}$ in the expression for n. Futhermore, $\hbar\vec{q}$ plays the same role in the case of phonons as $\vec{p}$ ($=m\vec{v}$) in the case of gas atoms; both determine the phase space accessible to the respective systems.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Self-Diffusion in fcc γ- and bcc δ-Cerium

M. P. Dariel and D. Dayan
Nuclear Research Centre-Negev, Beer-Sheva, Israel
and
A. Languille
Centre d'Etudes Nucleaires, Fontenay-aux-Roses, 92, France

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The serial sectioning method was used to study self-diffusion in cerium metal. In the fcc γ phase, $D=0.6e^{-36\,600/RT}$ cm^2 sec^{-1}, and in the bcc δ phase, $D=1.2\times10^{-2}e^{-21\,500/RT}$ cm^2 sec^{-1}. The diffusion parameters in the fcc structure are compatible with a normal vacancy mechanism. The high diffusivities and low activation energy in the bcc phase are characteristic of diffusion behavior in anomalous bcc metals. Similarities with self-diffusion in bcc ϵ-plutonium are stressed.

INTRODUCTION

The diffusion behavior of the anomalous bcc metals has attracted considerable attention in the last several years. It is well established[1] that a number of bcc metals possess unusual properties with regard to self-diffusion and impurity diffusion. No single explanation[2-4] of the anomalous properties has yet completely been accepted.

β-titanium,[5] β-zirconium,[6] and γ-uranium[7] were originally considered as anomalous bcc metals. The bcc structure of these metals extends over a temperature range of several hundred degrees. It was therefore possible to detect a definite curvature of the Arrhenius plots for both, self- and solute diffusion. The activation energies for self-diffusion in the lower temperature range of the bcc phase had unusually low values, contrary to the usually obeyed semiempirical rules. Furthermore, the extremely low preexponential terms indicated negative entropies of activation.

More recently it has been shown that also β-hafnium,[8] ϵ-plutonium,[9] and β-praseodymium[10] have some of the characteristic features of the anomalous bcc metals. The bcc structure in this group extends only over a narrow range of temperatures, thus precluding the detection of curved Arrhenius plots. The activation energies, however, have anomalously low values. The preexponential terms, though low, are less anomalous than those of β-Zr and β-Ti.

bcc structures were found in seven other rare-earth metals in addition to praseodymium, either as the only existing solid allotropic form or as high-temperature structures. Information concerning the diffusion behavior of these metals is very scarce. This is due to the unavailability of metals of sufficient purity and to the difficulties involved in diffusion studies with highly reactive materials.

Self-diffusion in the high-temperature bcc phase of plutonium has been studied at normal[9] and at high pressures up to 12 kbar.[11] In contrast to most metals, the self-diffusion coefficients in plutonium increase with increasing pressure. This fact was related to the negative slope of the liquidus in the P-T diagram of plutonium.[12] In order to explain the negative volume of activation, a model was proposed[11] according to which the atom in the activated state has a different electronic configuration and therefore a different size than the atoms at ordinary lattice positions. The activated atoms move into octahedral interstitial sites in the lattice. This electronic configuration was tentatively identified as being that of plutonium in the liquid state.

The metal cerium has a stable fcc structure from - 10 to 720°C. It then transforms to the bcc form which subsists up to the melting point at about 800°C. According to the pressure-temperature diagram of cerium,[13] the slope of the liquidus is negative, similar to that of plutonium.

The behavior of plutonium and cerium is outstanding in the sense that there is an increase of density upon transformation from a bcc metallic phase to the liquid state. Jayaraman[13] suggested that the passage from bcc to liquid cerium involves a $4f \rightarrow 5d$ electron promotion and consequently a collapse of the atoms to a smaller size. The energy level of the single f electron is very close to the conduction band. It has often been observed, that cerium in various compounds or alloys is in the tetravalent state contrary to most rare earths which are trivalent.

The object of the present study was to provide experimental data concerning the self-diffusion in the fcc γ and the bcc δ phases. If as anticipated, the anomalous diffusion behavior of cerium were borne out by the experimental results, it would be instructive to compare it to the behavior of other anomalous bcc metals. Measurement of the self-diffusion coefficients at normal pressure constitutes the first step towards high-pressure experiments being carried out at present.

Another motivation for this research is connected with the problem of fast diffusion of certain solutes in lanthanum[14] and preaseodymium.[15,16] The characteristic features of this fast diffusion are similar to the previously observed ultrafast diffusion of noble-metal solutes in III*B* and IV*B* metals.[17] It was decided to extend these studies to other rare-earth metals, and in the first place to cerium. Cerium is suitable for such studies because it is the only rare-earth metal (with the exception of lanthanum) that has two consecutive cubic phases. It is therefore possible to study diffusion in isotropic media of different crystalline structures. Self-diffusion measurements are an obvious prerequisite in order to provide the necessary reference for the solute diffusion studies to be carried out later.

EXPERIMENTAL

Materials and Tracers

Several samples of cerium metal from different sources were examined by metallographic and spectrochemic analysis. Variations of the impurity content, exceeding 0.1%, were detected even though the metals had been specified to be more than 99.9 wt% pure. The purest metal available was supplied by Rare-Earth Products Ltd., England, and was therefore exclusively used in the present studies. The metallic impurity content, determined by spectroscopic analysis, is shown in Table I. Oxygen (400 ppm) and carbon content (300 ppm) were determined by vacuum fusion. The observed oxygen concentration was much higher than the solubility of oxygen in cerium. Excess oxygen appeared in the form of oxide inclusions, easily observable by metallographic examination.

Previous diffusion studies in rare-earth metals[15,16] have shown that the most effective method for tracer deposition was by vacuum evaporation of metallic tracers. Small amounts of cerium of the same stock as that used for sample preparation were neutron irradiated. Cerium of natural isotopic abundance contains several stable isotopes which, upon neutron irradiation, decay by various decay schemes, involving daughter products other than cerium isotopes. The most abundant stable cerium isotope (88.5%) is Ce^{140}. After neutron capture its product, Ce^{141} decays with a half-life of 32.5 days to stable Pr^{141}, emitting a 145-keV γ ray. The other radioactive isotopes are either short lived or emit in other energy ranges that can be discriminated from the one at 145 keV. The irradiated cerium tracers, after a decay period of 2 weeks, were examined in a multichannel γ analyzer. No tracers of radioactive impurities were detected and the 145-keV peak could easily be resolved. This peak was used in the subsequent specific activity determinations.

Sample Preparation

After removal of the surface oxide layer, the cerium lumps were melted and cast into high-purity magnesia crucibles in an induction furnace in purified argon atmosphere. The cast ingots were machined into cylindrical samples (10-mm diam, 7-8 mm high) with plane-parallel faces. The planar

TABLE I. Impurity content of cerium. Cerium metal was stated by the supplier to contain 200 ppm of other rare-earth metals.

Impurity	Conc. (ppm)
Fe	20
Mg	<10
Mn	5
Al	<10
Cu	<5
Pb	<5
Zn	<10
Sn	<5
Ni	<10
Si	<10

surfaces were carefully ground, polished on Microcloth impregnated with progressively finer diamond paste, and etched to remove the disturbed surface layer. The samples were then annealed at 680 °C for 48 h in evacuated and sealed quartz capsules. In the room-temperature stable fcc phase, this yielded an average grain diameter of 3 mm. The oxide inclusions were distributed along the grain boundaries. The grain size of the samples during the high-temperature diffusion anneal in the bcc phase is not known. However, it was observed that grain growth in cerium was fast.

In order to remove the slight oxide layer formed during grain growth, one of the sample faces was swab etched in a solution containing equal volumes of concentrated nitric acid, glacial acetic acid, and glycerine. The sample was then rinsed with alcohol and dried. Three similarly prepared cerium samples were placed in a sample holder, with their cleaned surfaces exposed 5 cm above a tantalum cup containing 20–30 mg of irradiated cerium. The whole assembly was placed in a vacuum system, evacuated to better than 2×10^{-6} mm Hg. The tantalum cup was heated by high-frequency induction to 1600 °C, the cerium evaporated within a few seconds. Activities of the order of 6×10^{4} count/min, in the energy range corresponding to the 145-keV γ ray, were thus obtained on each sample.

Annealing, Sectioning, and Counting

The tracer-coated samples were wrapped in tantalum foils and sealed in quartz capsules evacuated to less than 10^{-5} mm Hg. The quartz capsules, in close contact with the tip of a Pt-Pt 13-Rh thermocouple, were inserted into a massive nickel block at the center of a horizontal tube furnace. During the diffusion anneal the temperature was kept constant to within 1 °C. The detailed procedure for reducing the heating-up time has been described elsewhere.[15]

A high-precision Schaublin-70 lathe was used for the serial sectioning of the samples. The pyrophoricity of cerium requires copious lubrication of the sample during cutting, if carried out under ordinary atmosphere. In order to circumvent this difficulty and also avoid the necessity of having to work in an inert-atmosphere glove box, a small cylindrical Perspex box was mounted on the lathe. This box was connected to an argon inlet and to a vacuum suction pump. The cerium chips were driven by the argon flow and collected in a small stainless-steel container on a 325 mesh nylon cloth supported on a copper grid. The steel container snugly fitted the interior of the Perspex box. The cutting tool reached the sample through a lateral slit in the Perspex cylinder. Starting the lathe motor simultaneously opened an electromagnetic valve controlling the argon flow. At the same time the vacuum suction pump was also started. This procedure enabled the recovery of 99.5% of the removed chips and effectively prevented their ignition.

Prior to sectioning, the diameter of the samples was reduced by about 1 mm. For samples diffusion annealed in the bcc phase, this decrease is less than that recommended for complete elimination of possible surface diffusion effects. As a consequence of the limited tracer activity that could be deposited by vacuum evaporation, a larger decrease of the sample diameter would have resulted in a prohibitive large decrease of the weight of the sections and hence of their activity. The thickness of each layer was determined from its weight (weighed with an accuracy of ± 0.02 mg), the known diameter of the sample, and its measured density. The density was determined by the liquid displacement method in monobromobenzene. The collected chips were placed in glass vials of uniform wall thickness and dissolved in 1cc of dilute nitric acid. A well-type 1-in. NaI (Tl) crystal served for counting. The single-channel analyzer window delimited the 145-keV energy range of the Ce^{141} photopeak. At least 10 000 counts were taken from each section. Corrections were made for the background, but none for dead time and decay, since these were negligible.

RESULTS

The solution of the diffusion equation with the thin-layer initial boundary conditions is given by

$$C(x,t)=W_0(\pi DT)^{-1/2}\,e^{-x^2/4Dt}\ ,$$

where W_0 is the total tracer quantity deposited on the surface layer. This solution gives straight C-vs-x^2 plots as shown in Fig. 1. In a few instances an anomalous high specific activity of the first section was observed. This anomaly never extended deeper than the first section; it was attributed to some tracer hold up in the very slight surface oxide barrier, formed either during tracer evaporation or during the subsequent diffusion anneal. No deviations due to short-circuiting effects were observed even at the deepest penetrations. Owing to the low initial activity, it was not possible to follow the decrease of the specific activity of samples annealed in the fcc phase, over more than two orders of magnitude at most.

Since the diffusion anneals in the high-temperature bcc phase were relatively short (2 h), non-negligible errors were introduced by the heating-up time. The effective diffusion anneal time was calculated using the iterative procedure described by Lai.[18] The diffusion coefficients, given in Table II, were determined with a precision of 2%, the estimated uncertainty of the temperature measurements is ± 1°. The temperature dependence of the

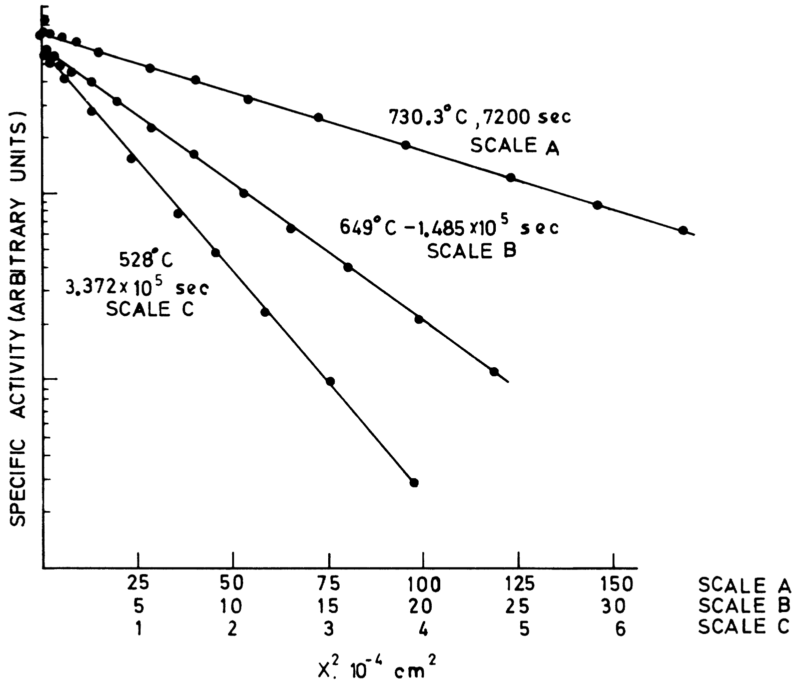

FIG. 1. Penetration profiles of Ce^{141} in fcc and bcc cerium.

self-diffusion coefficients in the two structures is shown in Fig. 2. The activation energies and pre-exponential terms, deduced from the straight Arrhenius plots, are given in Table III.

DISCUSSION

Self-Diffusion in fcc γ-Cerium

The samples used for diffusion studies in the fcc phase had a relatively large grain size of 3 mm average diameter. Straight penetration plots were obtained with the decrease of specific activity extending over two orders of magnitude. The results were therefore considered representative of true bulk diffusion.

TABLE II. Self-diffusion coefficients of cerium.

Temperature (°C)	Phase	D ($\mathrm{cm^2\ sec^{-1}}$)
528.0	fcc	5.44×10^{-11}
553.5	fcc	1.13×10^{-10}
575.2	fcc	2.04×10^{-10}
606.8	fcc	4.00×10^{-10}
634.0	fcc	8.31×10^{-10}
634.0	fcc	8.54×10^{-10}
649.0	fcc	1.01×10^{-9}
670.6	fcc	1.79×10^{-9}
670.6	fcc	1.71×10^{-9}
692.0	fcc	2.93×10^{-9}
719.4	bcc[a]	2.04×10^{-7}
730.3	bcc	2.49×10^{-7}
732.0	bcc	2.54×10^{-7}
740.4	bcc	2.64×10^{-7}
742.1	bcc	2.72×10^{-7}
748.0	bcc	2.82×10^{-7}
760.3	bcc	3.28×10^{-7}
762.0	bcc	3.38×10^{-7}
771.4	bcc	3.73×10^{-7}

[a] The diffusion anneal of all samples in the bcc was 2 h.

The measured value of the activation energy in γ-cerium, $Q = 36\,600$ cal/mole is in excellent agreement with the semiempirical rule $Q = 34T_m$. This expression yields $Q = 36\,300$ cal/mole using a hypothetical melting temperature for γ-cerium,[19] $T_m = 1068\ ^\circ\mathrm{K}$. Assuming a vacancy-controlled mechanism for self-diffusion, one can write

$$D_0 = \beta a^2 f \bar{\nu}\, e^{\Delta S/R}\ , \tag{1}$$

where $\beta = 1$ for cubic metals, a is the lattice parameter (5.16 Å), f is the correlation factor (0.78), and the Debye frequency $\bar{\nu} = 3\times10^{12}\ \mathrm{sec^{-1}}$.[20] Using the experimental value $D_0 = 0.6\ \mathrm{cm^2\ sec^{-1}}$, one obtains $\Delta S = 9.1$ e.u./mole.

According to Zener,[21] ΔS can be expressed by

$$S = \lambda\theta Q/T_m\ , \tag{2}$$

where $\lambda = 0.55$ for vacancy mechanism and

$$\theta \simeq -\frac{d(\mu/\mu_0)}{d(T/T_m)}\ ,$$

with μ/μ_0 the normalized shear modulus. For cerium $\theta = 0.5$, as determined by interpolation in the respective values of other rare-earth metals.[22] Substituting these values into Eq. (2) one finds ΔS

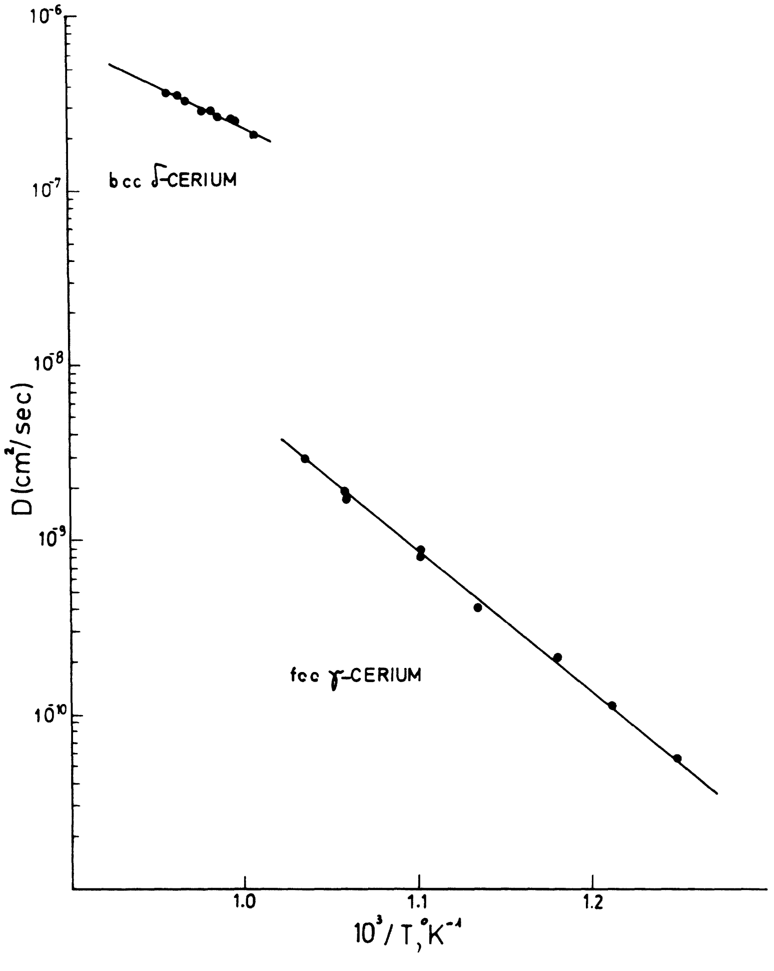

FIG. 2. Temperature dependence of the self-diffusion coefficients in fcc and bcc cerium.

$= 9$ e.u./mole in good agreement with the experimental ΔS.

It follows that insofar as self-diffusion, γ-cerium behaves like a normal fcc metal. It was shown[14] that a similar situation prevails in β-lanthanum.

Self-Diffusion in bcc δ-Cerium

The self-diffusion coefficients increase by a factor of 40 upon transformation from the close-packed fcc to the bcc structure. Similar behavior was observed in most metals showing a close-packed fcc to bcc transformation. This was attributed to the greater mobility of the defects which are responsible for diffusion in the more loosely packed bcc structure.

The diffusivities of cerium near its melting point, 4×10^{-7} cm²/sec⁻¹, are remarkably high. Lazarus[23] pointed out that if one plots log D vs T_m/T, the experimentally observed diffusion coefficients of the bcc metals, fall into two bands. For the normal bcc metals, D at T_m is about 5×10^{-8} cm²/sec⁻¹ whereas for the anomalous bcc metals, tenfold higher values were observed.

The measured activation energy for bcc cerium, 21 500 cal/mode, is anomalously low. The present cases $Q/T_m = 20$ instead of the usual value of 34. This is one of the characteristic features of the anomalous bcc metals. The activation entropy on the other hand, even though low, is nevertheless positive, $\Delta S = 1.7$ e.u./mole. A similar behavior was found for the self-diffusion parameters of praseodymium,[10] another rare-earth metal.

In view of the high diffusivities and low activation energies on one hand, and the quasinormal activation entropy on the other, cerium, praseodymium,

TABLE III. Self-diffusion parameters in cerium.

Phase	Q (kcal/mole)	D_0 (cm² sec⁻¹)
fcc	36.6 ± 0.4	$\left(5.5\pm^{1.3}_{1.1}\right)\times10^{-1}$
bcc	21.5 ± 0.7	$\left(1.2\pm^{0.5}_{0.4}\right)\times10^{-2}$

and possibly the other bcc allotropes of the rare-earth metals, seem to occupy an intermediate position between the anomalous and the normal bcc metals.

Peart and Askill[4] tried to account for diffusion in anomalous bcc metals by a combination of vacancy-divacancy diffusion with an additional contribution due to the dislocation network. In the present case, the anomalous low activation energy was observed in the bcc phase which extends over a temperature range of $T > 0.9T_m$. At these elevated temperatures it is unlikely that short-circuiting diffusion along the dislocation network will contribute significantly to the over-all bulk diffusion. However, it is not unlikely that, immediately following the phase change during the heating up time to the annealing temperature, there might be a Gaussian contribution of diffusion due to rapid grain growth of the dislocation network. According to Peart and Askill[4] the excess dislocations generated by the phase change are annealed out in the relatively short period of < 1 h and form stable subgrain networks. Therefore the measured diffusion coefficient is expected to be a decreasing function of the duration of the anneal, at a given temperature. In order to check this possibility, three samples were diffusion annealed at 724 °C, just above the transformation temperature for 1200, 3100, and 10 800 sec, respectively. After correcting for heating-up time, it was found that the diffusion coefficients indeed decrease with annealing time. The value of the self-diffusion coefficient of the sample annealed for the shortest period was 15% higher than that of the sample annealed for 3 h. This difference is significantly greater than the experimental uncertainty involved in the determination of the diffusion coefficients.

It follows that the dislocation network generated by the phase transformation contributes, albeit to a limited extent, to the diffusivities. The anomalous low activation energy, however, still seems to be a characteristic feature of bulk diffusion and cannot be accounted for only on the basis of diffusion due to the presence of dislocations.

One should also consider the diffusion mechanism that has been proposed in conjunction with ε-plutonium.[11] There are certain striking similarities between plutonium and cerium. In particular both metals have negative volumes of melting, and accordingly negative liquidus slopes in their P-T diagrams. Furthermore, both in cerium and in plutonium the more loosely packed bcc structures have a higher density than the respective close-packed fcc phases. The self-diffusion parameters in bcc ε-plutonium at normal pressure are similar to those found in the present study for δ-cerium. Diffusion studies at pressures up to 12 kbar showed a negative volume of activation. In order to account for these results, Cornet[11] proposed that self-diffusion in ε-bcc-phase takes place via an "activated" intersitialcy mechanism. Tha activated atoms at interstitial positions are presumed to have a different electronic structure than those at normal lattice sites. Assuming a transfer of two electrons per ion to the conduction band, the activated ions have a valency of 7^+ and an ionic radius of 1.4 Å. Using elastic theory calculations Cornet was able to obtain a reasonable agreement with the high-pressure diffusion results and in particular with the negative volume of activation.

Since this model for the mechanism for self-diffusion in ε-plutonium is based on Jayaraman's theory[13] for the negative volume of melting in cerium, it seems appropriate to apply it to the self-diffusion in this metal. A model based on electron transfer in cerium is plausible. In addition to Jayaraman's theory for melting, the low-temperature phase transformations of cerium[24] are also explained in terms of an electron transfer from the $4f$ state to the conduction band. A quantitative application of this model is, however, still premature, since it requires the results of the high-pressure experiments to be carried out shortly.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Self-Consistent Average Green's Function in Random Lattices: A Generalized Coherent-Potential Approximation (n) and Its Diagrammatic Equivalents*

B. G. Nickel and J. A. Krumhansl
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

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We describe a simple generalization of the coherent-potential approximation that is *exactly* equivalent to the self-contained cumulant expansions and the self-consistent diagrammatic-resummation techniques. A detailed analysis of these different methods for the pair case is given.

I. INTRODUCTION

Much of the recent work in disordered-model alloy problems has been concerned with the calculation of the average Green's functions. Since this calculation can be done exactly for only one special model,[1] attempts have been made to develop a systematic scheme which can be used to obtain a sequence of improving approximations. Notable among these techniques are the cumulant expansions of Yonezawa and Matsubara,[2] the corrected or self-contained cumulant expansions of Yonezawa,[3] and, paralleling this latter development, the diagrammatic expansion of Leath[4] and Leath and Goodman.[5] A rather different approach is suggested by the coherent-potential approximation (CPA) of Soven[6] for electronic states, the self-consistent method of Taylor[7] for vibrational excitations, and the treatment of excitons by Onondera and Toyozawa,[8] all of which are formally identical and can be considered as good first approximations.

The diagrammatic (or corrected-cumulant) approaches are appealing in the sense that one can "visualize" the approximations that are made and they can, in principle, be used to obtain a sequence of improving results. In practice, however, the solution of the counting problem has proved very elusive and so far only the lowest-order or so-called "single-site" approximation has been correctly obtained and applied. Thus although previous attempts have been made to calculate the next-order or "pair" approximation, these calculations have been either incomplete or have contained significant errors.[9,10] We will make additional comments on these last two calculations later in an attempt to relate them to the present development.

The CPA calculation has been shown to be exactly equivalent to the single-site corrected-cumulant approximation mentioned above.[4] However, it is not obvious how one would generalize the method in the "best" possible way—formal generalizations of course exist,[11,12] but none of the approximation schemes that have been developed[13] have actually led to a generalization that has the (simple) equivalence to the corrected-cumulant or diagrammatic expansions possessed by the elementary CPA.

What we show below is that there does exist a generalization of CPA such that CPA (n) is exactly equivalent to the n-site corrected-cumulant or diagrammatic approximation. This generalization is quite straighforward in any order but for simplicity we restrict ourselves mainly to CPA (2) or the pair approximation. It is also of interest to note that the method outlined below can be easily extended to obtain a systematic sequence of approximations for the average two-particle Green's function.

A very convenient model system, which we use as the basis for our discussion, is described in Sec. II. Although some extensions of this model are obviously possible without substantially modifying our generalization of the CPA, we have not made any detailed analysis to determine exactly what aspects of the CPA (n) are specifically model dependent. In Sec. III we outline the cumulant and corrected-cumulant techniques of Matsubara and Yonezawa[2,3] and then in Sec. IV we review the diagrammatic summation technique of Leath[4] and use it to derive