

a trivial matter. X-ray emission measurements have been made¹³ on related compounds and different Mg-Al alloys, and the emission bands corresponding to electron recombination between valence band and *L* shells of Mg or Al have not at all reflected a similar situation. In both cases, the soft-x-ray spectra of the alloys indicated that one fraction of the valence band electrons recombined with the Al core and another—with a different energy distribution—with the Mg core. This difference is not due to orbital selection rules which govern the soft-x-ray emission.

We were able to examine the total valence-band density of states with Auger electrons. The results were very similar to those obtained with x-ray and uv photoemission. Similar electron-emission measurements for Mg₂Ge and Mg₂Si, together with the energies of the core levels of all these materials, will be reported in a future publication.¹⁰

It has been shown that the x-ray and uv photoemission and Auger-emission curves are similar for Mg₂Sn, suggesting that each represents rather well the density of states of the bulk material.

We thank Dr. E. Schönherr for preparing the Mg₂Sn sputtering target and Mr. G. Krutina for

assistance in the measurements.

*On leave from the U. S. Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

¹D. W. Langer, *Z. Naturforsch.* **24a**, 1555 (1969).

²L. Ley, S. Kowalczyk, R. Pollak, and D. A. Shirley, *Phys. Rev. Lett.* **29**, 1088 (1972).

³N. V. Smith, *Crit. Rev. Solid State Sci.* **2**, 45 (1971).

⁴D. E. Eastman and W. D. Grobman, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors*, Warsaw, Poland, 1972 (to be published).

⁵N. J. Shevchik, J. Tejada, C. M. Penchina, and M. Cardona, to be published.

⁶D. E. Eastman and W. D. Grobman, *Phys. Rev. Lett.* **28**, 1327 (1972).

⁷C. C. Chang, *Surface Sci.* **25**, 53 (1971).

⁸H. G. Maguire and P. D. Augustus, *J. Phys. C: Proc. Phys. Soc., London* **4**, L174 (1971).

⁹C. J. Powell and A. Mandl, *Phys. Rev. Lett.* **29**, 1153 (1972).

¹⁰J. Tejada, N. J. Shevchik, D. W. Langer, and M. Cardona, to be published.

¹¹M. Y. Au-Young and M. L. Cohen, *Phys. Rev.* **178**, 1358 (1969).

¹²C. J. Powell, *Appl. Phys. Lett.* **20**, 335 (1972).

¹³A. Appleton and C. Curry, *Phil. Mag.* **12**, 245 (1965).

Problems in Strong-Scattering Binary Alloys*

Bernie G. Nickel†

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

and

William H. Butler

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 9 November 1972)

We present results of model calculations based on two different approximations which were both intended to be improvements over the coherent potential approximation. We show that both approximations yield nonphysical solutions; specifically, they predict average Green's functions which contain singularities on both the upper and lower halves of the complex energy plane. We conjecture that nonanalytic behavior will occur generally in high-order approximations to the average Green's function.

We report numerical calculations based on two very different extensions of the coherent potential approximation (CPA). One is based on the corrected cumulant scheme of Yonezawa¹ as developed by Nickel and Krumhansl²; the other is based on the cluster approach of Butler and Kohn³ developed to include self-consistency as outlined

by Butler.⁴ Our calculations of the average Green's function for binary alloys are carried out not only for real energies but for complex energies as well. It is this extension into the complex energy plane that makes these calculations unique and shows absolutely unambiguously that the solutions of the equations for the average

Green's function within both approximations contain nonanalyticities off the real energy axis. The nonanalyticities are branch points in both the upper and lower halves of the complex energy plane and are clearly nonphysical. We conjecture that these nonanalyticities are a general feature of extensions of the CPA. For this reason we suggest that proposed formal approximations be treated with caution until their analytic behavior is understood.

Before we actually describe the numerical calculations we outline what we feel are the most important points to be learned from this calculation. Some of these points may appear trivial; however, we feel that in the past their significance has been overlooked.

(1) The exact average Green's function is analytic in the complex energy plane except for a cut along the real axis. That is, because every exact Green's function contributing to the average has singularities only on the real axis, one can show that the average and all its derivatives are necessarily bounded off the real axis. Note, however that here and below we confine our discussion to the "physical sheet" defined by the boundary condition $G(E) \sim E^{-1}$, $E \rightarrow \infty$, and the reality condition $G^*(E) = G(E^*)$. We say nothing about singularities which appear in general on other branches of $G(E)$.

(2) Nonanalyticity (by which we specifically mean nonanalyticity off the real energy axis) makes the approximation unacceptable. Nonanalyticity implies such physically nonsensical space and time behavior of the Green's function as solutions growing in time. Also, local properties such as the density of states can no longer be uniquely defined, and furthermore sum rules, such as expressions for the integrated density of states, are no longer satisfied.

(3) There is no *a priori* reason to expect that an arbitrary approximation to the exact average Green's function will be analytic. Analyticity appears very hard to establish generally; we know of only one approximation scheme for which a general proof has been found.⁵

Note that analyticity has never been proved for the single-site CPA except for certain special models. On the other hand the CPA has been used very extensively and no counter example has ever been found—suggesting that a proof of analyticity might exist. The work of Tsukada⁶ and one of us⁶ is particularly relevant here. These model calculations involve partitioning the

system into "molecular" clusters and performing a simple CPA calculation with these clusters as a "single-site" basis.⁷ Fairly extensive searches in the parameter space of potential strengths and concentration have not turned up any nonanalyticities.⁸

(4) The calculations presented here are based on two entirely different formalisms and approximations. Their only points in common are that they are both attempts to go beyond the CPA to take into account the effects of fluctuations and that they are both self-consistent theories in the sense that the calculated average Green's function is used in the defining equation for the self-energy employed in the calculation. Because of this we feel that analyticity problems in other self-consistent high-order approximations will be the rule rather than the exception. Additional evidence comes from the numerical work of Capek⁹ based on yet another approximation scheme.

It is important to realize that the approximations discussed here *do* yield analytical results for certain choices of the alloy parameters and even when nonanalyticity appears, often very reasonable density-of-states curves can be found. Thus we feel that published results based on other approximate formulations must be treated with caution—one needs to carry out a very extensive search in parameter space to discover whether one's approximation has *general* validity.

Corrected cumulant calculation.—We present below a calculation for a one-dimensional tight-binding system for a particular set of model parameters. Other calculations, both in one and three dimensions, have been performed; the single calculation presented here adequately describes the nature of the problem.

We consider the model Hamiltonian $H = \sum W_{ij} a_j \times a_i^\dagger + \sum \epsilon_i a_i^\dagger a_i$, where W_{ij} is translationally invariant and defines an unperturbed Green's function

$$g_{ij}(E) = (2\pi)^{-1} \int dk \exp(ikR_{ij}) [E - \cos(ka)]^{-1}.$$

Randomness is contained in ϵ_i which we take to be $\epsilon_+ = 1.75$ with probability $c = 0.25$ and $\epsilon_- = 0$ with probability $1 - c = 0.75$. Note that the band-splitting parameter $\delta = (\epsilon_+ - \epsilon_-)/(\text{half-bandwidth})$ equals 1.75; we are in a strong-scattering regime.

We use the corrected cumulant scheme described by Nickel and Krumhansl (NK) and truncate the self-energy at the level of pairs, nearest and next-nearest neighbor only. That is, we

take the self-energy to be

$$\begin{aligned} \Sigma(k) = & \Sigma_{00}^{(1)} + 2\Sigma_{00}^{(2)}(1) + 2\Sigma_{00}^{(2)}(2) \\ & + 2\Sigma_{01}^{(2)} \cos(ka) + 2\Sigma_{02}^{(2)} \cos(2ka). \end{aligned}$$

Our approximate average Green's function is then given by

$$\begin{aligned} \langle G \rangle_{ij} = & (2\pi)^{-1} \int dk \exp(ikR_{ij}) \\ & \times [E - \cos(ka) - \Sigma(k)]^{-1}. \end{aligned}$$

To obtain Σ we have to solve Eq. (22) in NK twice: once to obtain $\Sigma_{00}^{(1)} + \Sigma_{00}^{(2)}(1)$ and $\Sigma_{01}^{(2)}$ in terms of $\langle G \rangle_{00}$ and $\langle G \rangle_{01}$, and again to obtain $\Sigma_{00}^{(1)} + \Sigma_{00}^{(2)}(2)$ and $\Sigma_{02}^{(2)}$ in terms of $\langle G \rangle_{00}$ and $\langle G \rangle_{02}$. We must also solve the CPA(1) equation to obtain $\Sigma_{00}^{(1)}$ in terms of $\langle G \rangle_{00}$. These equations, in addition to the equations for $\Sigma(k)$ and $\langle G \rangle_{ij}$ given above, then completely define the problem. The numerical work is completely straightforward. We require the three matrix elements $\langle G \rangle_{00}$, $\langle G \rangle_{01}$, and $\langle G \rangle_{02}$, and these we obtain by iteration using a Newton-Raphson technique.

The equations are highly nonlinear and yield many solutions. We determine the correct solution by starting at a very large value of the energy where we know the asymptotic values of the quantities appearing in the equations. We then follow this unique solution towards the energy region of interest. The self-energy $\Sigma_{00}^{(1)}(E)$ obtained in this calculation is shown in Fig. 1 for a small region in the complex energy plane. Because of the existence of branch-point singularities off the real axis one is forced to introduce branch cuts to define a single-valued function $\Sigma_{00}^{(1)}(E)$. This is a largely arbitrary procedure; we have chosen to draw cuts perpendicular to the real axis. Note that $\langle G(E) \rangle_{00}$ necessarily has the same analytic structure and thus, for example, the density of states $[\text{Im}\langle G(E) \rangle_{00}]$ on the real axis will show step discontinuities.

We have already outlined why such behavior in $\Sigma(E)$ and $\langle G(E) \rangle$ is unsatisfactory. We now discuss to what extent it can be considered a general feature. First, when we truncated the self-energy at nearest-neighbor pairs only we could not find any nonanalyticities in this one-dimensional model but we did find them in a similar strong-scattering high-concentration regime in a three-dimensional simple-cubic model. If we extend the self-energy to include pairs out as far as eighth-nearest neighbor (in one-dimension) the nonanalyticities remain. Finally, they also occur if we include nearest- and next-nearest-

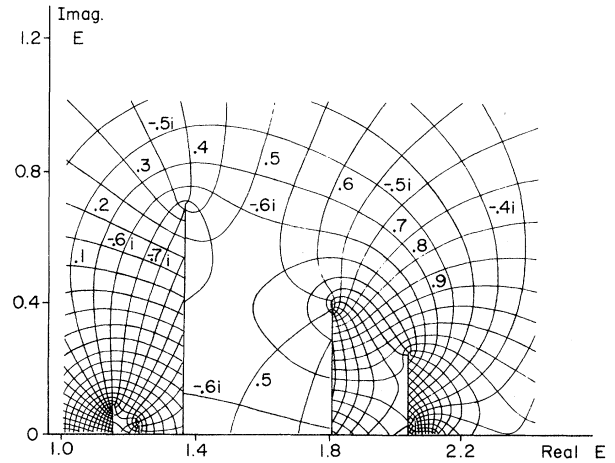


FIG. 1. Contours of equal real and imaginary parts of the self-energy in the pair approximation of NK. The solution has been chosen such that $\langle G(E) \rangle \approx E^{-1}$ for large E .

neighbor pairs and the close-packed triplet configuration in the self-energy. A large range of concentration and scattering strengths has not been investigated.

Self-consistent cluster calculation.—The calculation described below was based on the same model Hamiltonian as the corrected cumulant calculation described above. Although the nature and motivation of the approximations are quite different, similar off-axis singularities are observed for some concentrations and band splittings.

The scheme used in that of Ref. 4.¹⁰ The average density of states per site, $\text{Im}\langle G_{00} \rangle$, is calculated for a site at the center of a cluster. The sites within the cluster are treated exactly during the configurational average while those outside the cluster are described by an effective Hamiltonian, $H = \sum W_{ij} a_j^\dagger a_i + \sum \bar{E} a_i^\dagger a_i$.

Self-consistency is introduced by choosing \bar{E} so that the average density of states per site calculated for the site at the center of the cluster is equal to the density of states calculated for the medium; thus we choose $\langle G_{00} \rangle = \bar{G}_{00}$. Here \bar{G} is the Green's function calculated with self-energy \bar{E} on all sites.

Figure 2(a) shows the diagonal element of the Green's function, \bar{G}_{00} , calculated for a three-site cluster with $\epsilon_+ = 2$ and $\epsilon_- = 0$, both with probability 0.5. W is taken to be 0.5 so that the band-splitting parameter δ is 2. Note the branch point occurring for $\text{Re}E \approx 2.1$. Figures 2(b) and 2(c) compare the true density of states with that obtained from this approximation. The curve in

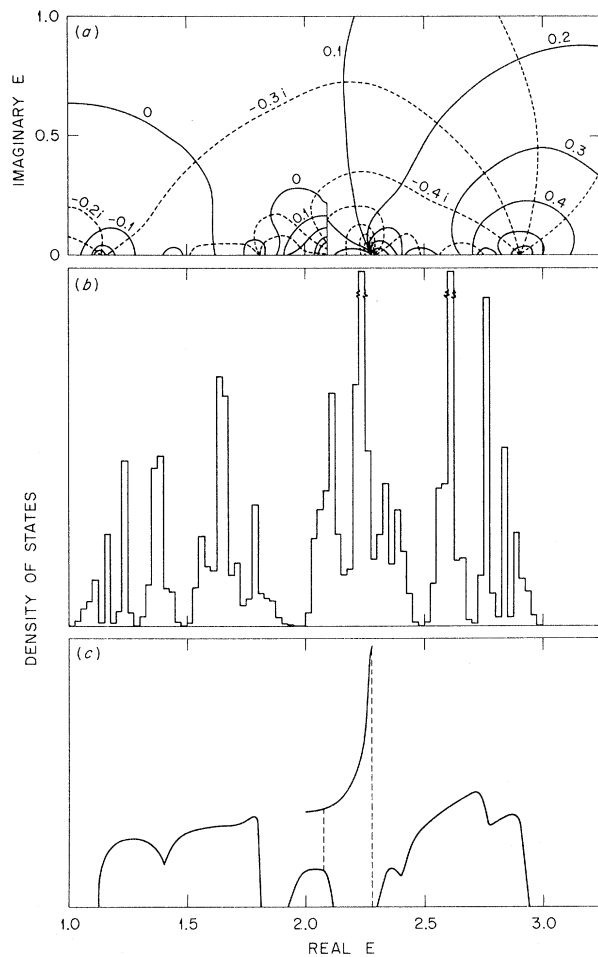


FIG. 2. (a) Contours of equal real and imaginary parts of the Green function \bar{G}_{00} in the self-consistent cluster approximation. The solution has been chosen such that $\bar{G}(E) \approx E^{-1}$ for large E . (b) Exact density of states. (c) Density of states from the self-consistent cluster approximation. The dashed line at $\text{Re}E \approx 2.1$ indicates where the branch cut has been drawn. The dashed line at $\text{Re}E \approx 2.3$ is due to an uncertainty in the density of states associated with singularity on the $\text{Re}E$ axis. The Green's function is continuous at $\text{Re}E \approx 2.3$ for $\text{Im}E$ slightly greater than zero.

2(c) was obtained by drawing the branch cut in G parallel to the $\text{Im}E$ axis.

We have investigated several values of δ as well as several concentrations and cluster sizes. Off-axis branch points are characteristic of large δ and high concentration. They exist for five-site clusters as well as for three sites. In the work of Ref. 4 branch points exist above the real energy axis at many of the peaks in the density of states. Difficulties in following, numerically, the solution to the self-consistent cluster equa-

tion through the peaks were not recognized as being due to off-axis branch points. The analytic problems of the self-consistent cluster approach and possible solutions to these difficulties will be discussed more fully in a subsequent publication.

Brouers, Cyrot, and Cyrot-Lackman¹⁰ have used the method of Ref. 4 (coupled with a further approximation which simplifies the numerical problems in three dimensions) to calculate the density of states of a model simple-cubic disordered alloy. When we repeated their calculation for a somewhat higher value of δ ($\delta = 2$) than the one they used we found regions in the complex E plane in which no solution could be obtained. This is not simply a numerical problem, but is related to the branch points which occur in the one-dimensional calculation. In our opinion the utility of the self-consistent cluster technique in three dimensions is still an open question which we hope to discuss further elsewhere.

Conclusions.—We feel that the results described above require a complete reappraisal of all methods based on averaging as used to date to describe excitations in random systems. In the hope of stimulating additional research we conjecture that self-consistency arbitrarily applied or equations of motion arbitrarily truncated will not work because one has not taken into account properly the interactions between different fluctuating components of the field, e.g., pair and triplet resonances in the corrected cumulant scheme, resonances in different spatially localized clusters in the cluster scheme. To be more specific, we note that the pair approximation of NK allows pair fluctuations throughout the crystal and also couples them all by introducing self-energy matrix elements between all possible pairs. The self-consistent cluster approach of Butler allows for fluctuations in only one region of the crystal and not elsewhere by forcing a medium description in terms of a single site-diagonal self-energy. Finally, the CPA of Tsukada again allows for fluctuations in all regions of the crystal but it specifically excludes any interactions by never introducing matrix elements of the self-energy between different “molecules.” Thus in some sense this “molecular” CPA appears as the mean; of course, it is not at all obvious that this has anything whatever to do with the fact that it seems to yield analytical results.

It is a pleasure to thank J. A. Krumhansl for discussions and suggestions throughout the course of this work. One of us (W.H.B.) would like to

thank J. S. Faulkner for helpful discussions.

*Work supported mainly by the U. S. Atomic Energy Commission through Contract No. AT(11-1)-3161.

†Present address: Department of Theoretical Physics, University of Oxford, 12 Parks Road, Oxford, OXI 3PQ, England.

¹F. Yonezawa, *Progr. Theoret. Phys.* **40**, 734 (1968).

²B. G. Nickel and J. A. Krumhansl, *Phys. Rev. B* **4**, 4354 (1971).

³W. H. Butler and W. Kohn, *J. Res. Nat. Bur. Stand., Sect. A* **74**, 443 (1970).

⁴W. H. Butler, *Phys. Lett.* **39A**, 203 (1972).

⁵R. H. Kraichnan, *J. Math. Phys. (N. Y.)* **2**, 124 (1961).

⁶M. Tsukada, *J. Phys. Soc. Jap.* **26**, 684 (1969); W. H.

Butler, unpublished.

⁷This approximation must be considered as a true CPA as compared with, say, the CPA(*n*) of Nickel and Krumhansl. The crucial distinguishing feature is that in this approximation there are *no* matrix elements of the self-energy linking different clusters.

⁸A 7% error in the total integrated density of states (suggestive of a branch cut) in the work of Tsukada has been checked by us and is apparently due to numerical error.

⁹V. Capek, *Phys. Status Solidi (b)* **43**, 61 (1971), and *Czech. J. Phys.* **B21**, 997 (1971).

¹⁰The same approximation appears to have been suggested independently by F. Brouers, M. Cyrot, and F. Cyrot-Lackman, to be published, and also by V. Capek, *Phys. Status Solidi (b)* **52**, 399 (1972).

Crystal-Field Effect on a Kondo System: Magnetic Susceptibility of La:Ce†

S. DeGennaro and E. Borchi

Istituto di Fisica dell'Università, Firenze 50125, Italy

(Received 18 September 1972)

In this paper we evaluate the effect of the cubic crystalline field on the magnetic susceptibility of the Kondo system La:Ce. We show the coexistence of the crystal-field splitting and the Kondo effect whenever the crystal field does not remove the degeneracy of the localized states completely. The theoretical curve is in good agreement with the experimental data for a choice of the Kondo temperature $T_K = 0.1$ K.

Recently there has been considerable work on low-temperature properties of cubic La:Ce. It is now well established that the La:Ce system behaves as a Kondo system. On the other hand, some uncertainty exists concerning the value of T_K , the Kondo temperature of the system. From resistivity measurements on La:Ce, Kim and Maple,¹ Gey and Umlauf,² Sugawara and Eguchi,³ and Wollan and Finnemore⁴ find the Kondo temperature T_K to be less than 1 K; similarly, from nuclear orientation studies Flouquet⁵ finds a Kondo temperature T_K of about 0.1 K, while Edelstein and co-workers^{6,7} from susceptibility measurements estimate T_K to be about 20 K.⁸ Edelstein⁷ analyzes experimental results using a phenomenological density of states for La:Ce. On the other hand, his tentative analysis in terms of a crystal field only⁶ fails just in the low-temperature region.

Evidence for the coexistence of the crystal-field splitting and the Kondo effect has been found by Yoshida and Sugawara^{9,10} in single crystals of Y:Ce. Others,¹¹⁻¹³ taking into account crystal-field splitting, showed the presence of sidebands in the resistivity of a Kondo system. A recent

analysis of the crystal-field effect on the resistivity has been made by Cornut and Coqblin,¹⁴ using the Schrieffer-Wolff transformation in the framework of the Anderson model, and by the present authors¹⁵ using the *s-f* exchange Hamiltonian. In this paper we calculate the magnetic susceptibility of the Kondo system La:Ce in the cubic phase, taking into account both crystal-field effects and the coupling between the local spin *J* and the conduction-electron spin *s*. The exchange interaction is conventionally written as $H_{sf} = -\Gamma \vec{J} \cdot \vec{s}$. Though the *s-f* exchange Hamiltonian has not had first-principles justification except when it can be derived from the Anderson Hamiltonian, it has been used extensively. Cornut and Coqblin¹⁴ find that applying the Schrieffer-Wolff transformation to the Anderson model leads to a Hamiltonian which is different than H_{sf} . We use H_{sf} for simplicity since it is still not completely clear which is the correct Hamiltonian. The use of this Hamiltonian appears to be well suited to the La:Ce case.^{15,16}

Separate contributions to the magnetic susceptibility from crystal-field and *s-d* (or *s-f*) interactions were calculated respectively by Murao