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Self-Consistent-Field Approximations in Disordered Alloys

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The connection between Taylor's recent self-consistent calculations of phonon frequency spectra in disordered alloys and those of Davies and Langer in the usual self-consistent-field approximation is established. It is found that Taylor's results are equivalent to summing the same diagrams summed by Davies and Langer, but with proper compensation against multiple occupancy of sites by defects. The recently developed technique of Elliot, Aiyer, and Leath, which self-consistently adjusts the diagram rules to obtain proper compensation, is used. This method is quite general and clearly can be used for other self-consistent calculations is disordered alloys.

RECENTLY, Taylor[1] has developed a self-consistent method, within the multiple scattering formalism of Lax,[2] for calculating phonon frequency spectra in mass-disordered alloys. His calculations at large defect concentrations produced results in quite good agreement with recent machine computations for a simple cubic lattice.[3] He also made a comparison of his self-consistent results for a linear chain with the earlier results of Davies and Langer[4] and reported a narrower impurity band that did not extend above the maximum frequency of the light lattice. The present author, using Davies and Langer's self-consistent-field approximation for a body-centered cubic crystal, found that a very broad impurity band was also obtained by this method in three-dimensional problems.[5] It seemed clear that Taylor's results were better than those produced by Davies and Langer's method but there was no obvious formal connection that would allow a more critical comparison. This paper makes that connection and, perhaps, suggests how further self-consistent calculations should proceed.

The connection will be established for the displacement Green's function D which gives the time-dependent displacement-displacement correlations.[6] It satisfies the equations of motion

$$(M\omega^2-V)D(\omega)=I\,, \tag{1}$$

where M is the diagonal mass matrix, and V is the force-constant matrix. In an alloy with mass matrix $M=M_A(I-\epsilon)$, where M_A is the mass of the A atoms and ϵ is the fractional mass defect matrix which is zero except at B atom sites, this equation becomes

$$(M_A\omega^2-V)D(\omega)=I+\mu D(\omega)\,, \tag{2}$$

where $\mu=M_A\epsilon\omega^2$. Upon multiplying from the left by $d(\omega)=(M_A\omega^2-V)^{-1}$, the A lattice propagator, iterating, and averaging over all configurations of the B atoms, we obtain

$$\langle D\rangle=d+d\langle\mu\rangle d+d\langle\mu d\mu\rangle d+\cdots. \tag{3}$$

The terms in this series can be classified by a set of diagrams[6] that were introduced by Langer.[7] The self-energy Σ satisfies the Dyson equation

$$\langle D\rangle=d+d\Sigma\langle D\rangle. \tag{4}$$

The simplest class of diagrams which contributes to Σ consists of the one-vertex diagrams which would be those shown in the first column of Fig. 1 if the propagator lines were unperturbed d lines. This direct one-vertex summation was carried out to first order in c, the concentration of B atoms, by Langer[7] with the result

$$\Sigma^{(1)}=cM_A\epsilon\omega^2/[1-M_A\epsilon\omega^2d_0]\,, \tag{5}$$

for the diagonal elements, where $d_0(\omega)=d(n\alpha,n\alpha,\omega)$ is the diagonal part of d in real space.

Davies and Langer's self-consistent-field approximation was essentially to substitute the diagonal part D_0 of the full propagator for d_0 in the denominator of (5). This procedure sums those diagrams shown in the first column of Fig. 1, where the cross-hatched double

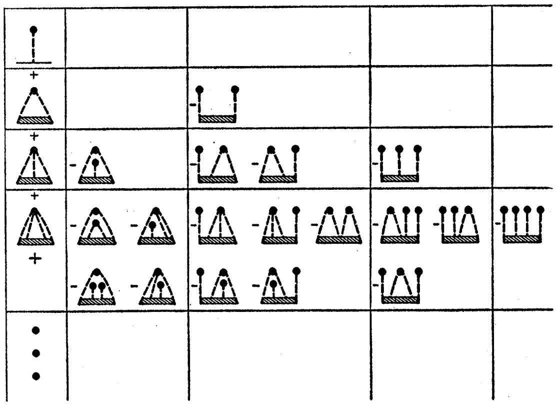

FIG. 1. The self-energy diagrams in the one-vertex self-consistent-field approximation with corrections for coincidence of defects.

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line represents the full propagator D_0. The result is

$$\Sigma_{\mathrm{DL}}^{(1)}=cM_A\epsilon\omega^2/[1-M_A\epsilon\omega^2D_0]. \tag{6}$$

In terms of d_0, many diagrams are summed, namely, all one-vertex diagrams with any number of one-vertex parts inserted between their interaction lines, where each of these one-vertex insertions itself has all similar insertions, etc.

Since the self-consistent-field approximation sums many diagrams, it seems likely that it should represent a better approximation to the exact result. Also the self-consistent field is physically reasonable in a random alloy since the phonon propagates between explicit interactions by way of the impure crystal. But, perhaps more important, the self-consistency gives the correct analytic properties to the self-energy, in particular, a branch cut along the impurity band.

What seems to be wrong with the naive summation (6) of these diagrams is that no compensation is made against multiple occupancy of sites by defects.[8] For example, the second diagram in the second row of Fig. 1 appears in the calculation of $\langle D\rangle$ with weight c^2 whenever the diagram in the first row is put into Σ with weight c. But, in the evaluation of $\langle D\rangle$, a summation is made over internal indices, and whenever the two sites coincide in the summation the diagram is weighted incorrectly since its weight then is only c. The correct weight c is put in by Davies and Langer's approach by including the first diagram in the second row in Σ, but the c^2 is not subtracted out. This can be done by subtracting from Σ the second diagram in the second row. The usual procedure has been to sum across the second row to obtain weight $(c-c^2)$ for the second-order vertex.[6] Similarly, if one sums across each row in Fig. 1 one obtains a multiple-occupancy polynomial $P_r(c)$ to associate with the rth-order vertex which corrects for defects coinciding on lattice sites in the summations. The straightforward procedure is the usual cluster expansion obtained by subtracting from c in each one-vertex diagram the weight of each diagram that can be obtained by breaking the vertex, and results in a combinatorial problem which can be solved in closed form for $P_r(c)$.[6] However, this procedure corrects for diagrams which do not appear explicitly in any particular approximation to Σ and leads to spurious behavior of Σ.[8] Thus, it seems that one must take care to include in the corrections only those diagrams which eventually appear in one's particular calculation. That is, the value $P_r(c)$ associated with each diagram is determined implicitly[9] by the diagrams that are to be summed. This feature can be incorporated by inspection or by induction in only the simplest cases. For example, the direct one-vertex calculation of Elliott and Taylor[10] has this feature.[8]

A more powerful implicit method must be used in general. Recently, Elliott *et al.* have developed such a method and applied it to the two-vertex summation.[11] The method is quite general and can be adapted to self-consistent calculations.

Instead of summing across each row in Fig. 1 to obtain $P_r(c)$ for each diagram, one sums down each column first to obtain σ_i and then across to obtain an implicit expression for Σ without learning the contribution of each diagram.

If we use this technique here, we find that the contribution from the first column in Fig. 1 is

$$\sigma_1=c\epsilon M_A\omega^2/(1-M_A\epsilon\omega^2D_0), \tag{7}$$

as obtained by Davies and Langer. The first concentration compensations come from the second column which contains all diagrams with one irreducible part but all possible explicit insertions. This contribution can be evaluated by treating $\Sigma=\Sigma[D_0]$ as a functional of its internal propagator. In terms of $\Sigma[D_0]$, these diagrams are $\Sigma[D_0/(1-\Sigma D_0)]$, minus the term with no insertions. That is, we write

$$\sigma_2=-\{\Sigma[D_0/(1-\Sigma D_0)]-\Sigma\}. \tag{8}$$

The minus sign occurs because the corrections are subtracted. Similarly, we find σ_3 to be

$$\sigma_3=-\Sigma[D_0/(1-\Sigma D_0)]D_0\Sigma[D_0/(1-\Sigma D_0)]. \tag{9}$$

The remaining columns are obtained similarly so that the final result for $\Sigma=\sum_{i=1}^{\infty}\sigma_i$ is

$$\Sigma=\frac{cM_A\epsilon\omega^2}{1-M_A\epsilon\omega^2D_0}-\frac{\Sigma[D_0/(1-\Sigma D_0)]}{1-\Sigma[D_0/(1-\Sigma D_0)]D_0}+\Sigma. \tag{10}$$

The last term on the right cancels the left-hand side so that the solution for $\Sigma[D_0/(1-\Sigma D_0)]$ is simply

$$\Sigma[D_0/(1-\Sigma D_0)]=cM_A\epsilon\omega^2/[1-(1-c)M_A\epsilon\omega^2D_0]. \tag{11}$$

In order to evaluate $\Sigma=\Sigma[D_0]$ we must make the replacement, in Eq. (11),

$$D_0/(1-\Sigma D_0)\rightarrow D_0$$

or

$$D_0\rightarrow D_0/(1+\Sigma D_0). \tag{12}$$

The result of this substitution in both sides of Eq. (11) is

$$\Sigma=cM_A\omega^2/\{1-(1-c)M_A\epsilon\omega^2[D_0/(1+\Sigma D_0)]\}. \tag{13}$$

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[8] For example, see a discussion of this point by P. L. Leath and B. Goodman (to be published).

[9] The word "implicit" here means self-consistent and is used to prevent confusion with the self-consistent-field approximation.

[10] R. J. Elliott and D. W. Taylor, Proc. Roy. Soc. (London) **296**, 161 (1967).

[11] R. J. Elliott, R. N. Aiyer, and P. L. Leath (to be published).

This self-consistent equation is the same as the one Taylor obtained by another method as can be seen by multiplying both sides by $(1+\Sigma D_0)^{-1}[1+\Sigma D_0-(1-c)\times M_A\epsilon\omega^2 D_0]$ to obtain

$$\Sigma(1+\Sigma D_0)^{-1}[1+\Sigma D_0-(1-c)M_A\epsilon\omega^2 D_0]=cM_A\epsilon\omega^2, \quad (14)$$

which is Eq. (3.7) of Taylor's paper.[1]

It now seems, with Taylor's calculations and this connection with the usual diagrams, that implicit compensation in diagrams is important. Furthermore, Yonezawa and Matsubara[12] have pointed out that any theory at large concentrations should be symmetric in the A- and B-atom types. Taylor has shown that Eq. (14) has this symmetry, so that implicit compensation also seems to restore A-B atom symmetry. A further feature of this method is that, with the resulting implicit equations in any calculation, the perturbation expansion is no longer a power series in c and can possibly yield results that are not analytic at $c=0$.

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Lattice Dynamics of Niobium-Molybdenum Alloys

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The frequency-versus-wave-vector dispersion relations for the normal modes of vibration of a series of alloys of the transition metals niobium and molybdenum have been measured at 296°K, and previous measurements on the pure metals have been extended, using coherent, one-phonon scattering of thermal neutrons. The phonon dispersion relations are very different for the two pure metals, suggesting that the electronic structure, acting through the electron-phonon interaction, plays a significant role in the determination of the dynamics of these materials. The observed neutron groups corresponding to the phonons in the alloys are not significantly broader than in the pure metals. The dependence of the dispersion curves on alloy composition is found to be complicated, both the general level of frequencies and the shape of the curves changing significantly. Fourier analysis indicates that the interatomic forces in the metals are oscillatory and of long range. Suspected Kohn anomalies are observed on several branches of the dispersion curves. With the assumption of a rigid-band model, the positions of several of these anomalies correlate with the calculated electron band structure for tungsten. The dimensions of the Fermi surface obtained from this correlation are in agreement with other Fermi-surface information.

1. INTRODUCTION

TRANSITION metals are characterized by a partially filled inner electronic shell. This unfilled shell results in many unusual properties[1] and might be expected to have a significant effect on the interatomic force system. This paper presents extensive measurements of the phonon dispersion curves of niobium and molybdenum and their alloys which demonstrate that such effects are quite marked. In favorable cases the results can yield information concerning the details of the electronic band structure.

The dispersion curves of the column-V transition metals niobium[2] (in the 4d series) and tantalum[3] (5d) show many similarities, as do those of the column-VI metals chromium[4] (3d), molybdenum[5] (4d), and tungsten[6] (5d). The dispersion curves of the column-V metals, however, differ greatly, both in shape and frequency level, from those of the column-VI metals.[7] Such effects imply a strong dependence of the interatomic forces on the electronic structure for these metals. Measurements of the dispersion curves of other metals[8] indicate that the interatomic forces in some are complicated while in others they are comparatively simple.

The electronic structures of the column-V and column-VI metals differ in that the column-V metals have five electrons outside the closed shell and the column-VI metals, six. Consequently, measurements of the phonon dispersion curves of a series of binary alloys of metals in columns V and VI in the same row should provide information on how the addition of d electrons to the unfilled shell changes the normal modes of vi-

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