PHYSICAL REVIEW B VOLUME 38, NUMBER 6 15 AUGUST 1988-II

Cluster coherent-potential approximation in ternary random alloys

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(Received 1 February 1988)

The augmented-space formalism introduced by one of us is used here to develop a self-consistent cluster coherent-potential approximation for the density of states for ternary random alloys. The approximation yields an averaged Green function which maintains its Herglotz properties for all energies and disorders. An application is made to a model for the ternary brass Cu-Ni-Zn.

I. INTRODUCTION

Recently we proposed a first-principles methodology to study the electronic properties of substitutional random binary alloys.[1] This augmented-space formalism (ASF) generalized the conventional coherent-potential approximation[2,3] (CPA) to include the effects of off-diagonal disorder, clustering, and short-ranged order. Unlike earlier approaches, the ASF maintains the Herglotz analytical properties for the single-particle propagator and the Ward identities for the vertex corrections to the response functions: properties essential for obtaining physical results. Related works are the traveling-cluster approximation[4] and the Herglotz, self-consistent approximation introduced by Kaplan *et al.*[5] also based on ASF. However, these are still to be implemented on realistic models. Extensions to the KKR (Korringa-Kohn-Rostoker) CPA method have been proposed.[6,7]

Most of the above implementation has been to binary alloys. Random ternary alloys form a class of systems of great interest: from ternary semiconductor alloys used in devices to brasses and stainless steels. Several single-site CPA or non-self-consistent embedded-cluster studies on ternary alloys have already appeared in the literature.[8–10] Our group has already studied a class of ternary alloys: the III-V semiconductor alloys like $Ga_xIn_{1-x}As$ and $GaIn_xSb_{1-x}$,[11] although in the bond-antibond basis we reduced the problem to a pseudobinary one. Here we wish to develop the formalism to the ternary brass system Cu-Ni-Zn.

We have taken Cu-Ni-Zn as the prototype ternary alloy in the same spirit as when we had chosen Cu-Ni as a prototype binary metallic alloy. It is a simple but interesting system where diagonal disorder dominates; the centers of the *d* bands of the three constituents are widely separated. Off-diagonal disorder, characterized by differences in constituent band widths, is small. It is well known that the single-site CPA begins to fail in alloys where we have a small concentration of one constituent whose band center differs from the *host* by amounts large compared with the bandwidths. This is certainly the case with Cu-Ni-Zn.

II. THE AUGMENTED SPACE FOR A TERNARY ALLOY

To introduce the basics of the formalism, let us concentrate on a *d*-band model within the tight-binding basis. The *d* states in a lattice with cubic symmetry can be categorized into t_{2g} and e_g symmetry components having, respectively, threefold and twofold degeneracies. The corresponding Hamiltonian is then a 2×2 matrix and may be written as

$$\underline{H}=\sum_{i,n} e_{in}\underline{P}_{in}+\sum_{i,n}\sum_{j,m} V_{in,jm}\underline{T}_{in,jm} \tag{1}$$

where e_{in} takes the values e_{An}, e_{Bn}, or e_{Cn} for the three different constituents. $n=1$ or 2 according to whether we are interested in the t_{2g} or e_g component. The Green function $G_{in,in}$ may be calculated as a continued fraction using the recursion method.[12] The coefficients are shown in Table I.

The ternary random occupation may be characterized by an *occupation variable* N_i, which takes the value 1, 0, or -1 according to whether the site labeled by i is occupied by the constituent atom labeled by A, B, or C. In the absence of short-range order we have the probability density of N_i as

$$P(N_i)=x_A(N_i-1)+x_B(N_i)+x_C(N_i+1)\ . \tag{2}$$

Mookerjee[3] suggested that one can now introduce a space ϕ_i on which the configurations of the variable N_i may be described. The basis $|f_n^i\rangle$ in this space describes the configurations of N_i whereas the probability density is related to an operator $\underline{M}_i$ through

$$P(N_i)=-\mathrm{Im}\langle f_0^i\,|\,(N_i\underline{I}-\underline{M}_i)^{-1}\,|\,f_0^i\rangle\ . \tag{3}$$

Note that $P(N_i)$ and $\underline{M}_i$ are the analog of the density of states and the Hamiltonian. In the case of the ternary distribution the rank of the space ϕ_i is 3. The method of constructing a representation of the matrix $\underline{M}_i$ has been described in some detail in Ref. 12. We first rewrite (2) as

$$P(N_i)=-\frac{1}{\pi}\mathrm{Im}\left[\frac{x_A}{n-1}+\frac{x_B}{n}+\frac{x_C}{n+1}\right],\quad n=N_i-i0^+$$

and expand the right-hand side as a continued fraction

$$\cfrac{1}{n-a_1-\cfrac{b_1^2}{n-a_2-\cfrac{b_2^2}{n-a_3}}}\ .$$

The representation of the matrix $\underline{M}_i$ is a 3×3 matrix and

TABLE I. Coefficients for the Green function $G_{in,in}$. Exponents are given in square brackets.

n	a_n	b_n^2	a_n	b_n^2
	Orbital 1		Orbital 4	
0	0.0	0.100 000[+01]	0.0	0.100 000[+01]
1	−0.736 282[−02]	0.295 643[−02]	−0.262 667[−02]	0.211 155[−02]
2	−0.285 673[−01]	0.235 335[−02]	−0.833 132[−02]	0.158 428[−02]
3	−0.160 718[−01]	0.179 840[−02]	−0.962 267[−02]	0.121 493[−02]
4	−0.134 218[−01]	0.162 690[−02]	−0.540 195[−02]	0.601 881[−03]
5	−0.112 190[−01]	0.156 254[−02]	−0.472 927[−02]	0.131 840[−02]
6	−0.131 124[−01]	0.174 530[−02]	−0.398 838[−02]	0.869 993[−03]
7	−0.671 958[−02]	0.153 999[−02]	−0.611 713[−02]	−0.895 845[−03]
8	−0.165 180[−01]	0.195 674[−02]	−0.219 311[−02]	0.854 633[−03]
9	−0.123 618[−01]	0.173 710[−02]	−0.107 605[−01]	0.126 003[−02]
10	0.0	0.168 461[−02]	0.0	0.125 162[−02]
	Orbital 2		Orbital 5	
0	0.0	0.100 000[+01]	0.0	0.100 000[+01]
1	−0.736 282[−02]	0.295 643[−02]	−0.262 665[−02]	0.211 155[−02]
2	−0.285 674[−01]	0.235 335[−02]	−0.833 131[−02]	0.158 428[−02]
3	−0.203 862[−01]	0.205 787[−02]	−0.116 066[−01]	0.121 205[−02]
4	−0.134 712[−01]	0.152 931[−02]	−0.128 611[−02]	0.610 331[−03]
5	0.907 024[−03]	0.164 361[−02]	−0.736 858[−02]	0.135 928[−02]
6	−0.596 882[−02]	0.155 990[−02]	−0.194 090[−02]	0.985 064[−03]
7	−0.463 769[−02]	0.131 672[−02]	−0.532 768[−02]	0.829 151[−03]
8	−0.128 520[−01]	0.134 450[−02]	0.453 185[−04]	0.955 998[−03]
9	0.128 076[−02]	0.160 917[−02]	−0.123 153[−01]	0.127 546[−02]
10	0.0	0.158 227[−02]	0.0	0.147 460[−02]
	Orbital 3			
0	0.0	0.100 000[+01]		
1	−0.736 282[−02]	0.295 643[−02]		
2	−0.285 673[−01]	0.235 335[−02]		
3	−0.203 862[−01]	0.205 787[−02]		
4	−0.134 712[−01]	0.152 932[−02]		
5	0.907 012[−03]	0.164 361[−02]		
6	−0.596 881[−02]	0.155 990[−02]		
7	−0.463 773[−02]	0.131 672[−02]		
8	−0.128 520[−01]	0.134 450[−02]		
9	0.128 075[−02]	0.160 917[−02]		
10	0.0	0.158 227[−02]		

in operator form it may be written as

$$\underline{M}_i = a_1 \underline{P}_1 + a_2 \underline{P}_0 + a_3 \underline{P}_{-1} + b_1(\underline{T}_{01} + \underline{T}_{10}) + b_2(\underline{T}_{1-1} + \underline{T}_{-11}) \tag{4}$$

where $\underline{P}$ and $\underline{T}$ are projection and transfer operators and the configuration states are labeled by 1, 0, and -1.

The next step is to replace the variables e_i and V_{ij} in terms of the their values for the three different constituents and the occupation variables. In the binary case, for example, we had $e_i = a + bN_i$ with $a = e_B$ and $b = (e_A - e_B)$. The relationship must contain two parameters which are then adjusted against e_A and e_B. In the ternary case we should have three parameters to adjust against the three values e_A, e_B, and e_C. The relationship should then be of the form $e_i = a + bN_i + cN_i^2$; the third term is an independent one, since unlike the binary case, N_i for the ternary case is no longer idempotent. We easily see from the above that $a = e_B$, $b = (e_A - e_C)/2$, and $c = (e_A + e_C - 2e_B)/2$.

Similarly, in the binary case we had $V_{ij} = A + B(N_i + N_j) + CN_iN_j$. The expression was symmetric in the two variables N_i and N_j and involved three parameters A, B, and C to be adjusted against the three parameters V_{AA}, V_{BB}, and V_{CC}. In the ternary case we have

$$V_{ij} = A + B(N_i + N_j) + CN_iN_j + D(N_i^2 + N_j^2) + E(N_iN_j^2 + N_jN_i^2) + FN_i^2N_j^2 \ .$$

This is symmetric in the labels i and j and involves six parameters to be adjusted against the six values taken by V_{ij}: V_{AA}, V_{BB}, V_{CC}, V_{AB}, and V_{AC}, and V_{BC}. The values of the parameters are shown in the Appendix.

The augmented-space Hamiltonian may now be constructed according to the recipe described in detail by Mookerjee[13] or Gray and Kaplan:[14]

$$\underline{\tilde{H}} = e_B \underline{I} \times \underline{I} + \sum_i \frac{(e_A - e_B)}{2} \underline{P}_i \times \underline{M}^{(i)} + \sum_i \frac{(e_A + e_C - 2e_B)}{2} \underline{P}_i \times (\underline{M}^{(i)})^2 + \sum_i \sum_j A\underline{T}_{ij} \times \underline{I}$$
$$+ \sum_i \sum_j B\underline{T}_{ij} \times (\underline{M}^{(i)} + \underline{M}^{(j)}) + \sum_i \sum_j C\underline{T}_{ij} \times \underline{M}^{(i)} \times \underline{M}^{(j)} + \sum_i \sum_j D\underline{T}_{ij} \times [(\underline{M}^{(i)})^2 + (\underline{M}^{(j)})^2]$$
$$+ \sum_i \sum_j E\underline{T}_{ij} \times [\underline{M}^{(i)} \times (\underline{M}^{(j)})^2 + (\underline{M}^{(i)})^2 \times \underline{M}^{(j)}] + \sum_i \sum_j F\underline{T}_{ij} \times (\underline{M}^{(i)})^2 \times (\underline{M}^{(j)})^2 .$$

The augmented-space theorem then gives

$$\bar{G}_{ij} = \langle iF_0 \,|\, (E\underline{\tilde{I}} - \underline{\tilde{H}})^{-1} \,|\, jF_0 \rangle . \quad (5)$$

So far, the treatment has been *exact.* We now begin the cluster approximation. We partition the augmented space into a subspace spanned by the n sites within the cluster and their 3^n configuration (C) and its complement C^*. We approximate the Hamiltonian in C^* by a translationally symmetric effective Hamiltonian to be self-consistently determined. We now use the partition theorem[15] to reduce the effective Hamiltonian to one only on the subspace C, by introducing a surface potential $S(K)$ to describe the effect of C^*. Finally we apply the partition theorem once more to reduce the Hamiltonian to a space c spanned by iF_0, $i = 1,2,\ldots,n$. From self-consistency this must be the effective Hamiltonian. The reduction is described in detail by Inglesfield[15] and Kumar *et al.*[1] The cluster CPA (CCPA) equation is of the form

$$\underline{\tilde{K}} = \underline{\tilde{H}}^{\,c} + \underline{P}_{F}0 \underline{\tilde{H}}^{\,C} \underline{G}^{c^*}(\tilde{K}) \tilde{H}^{\,C} P_F 0 .$$

$\underline{G}^{c^*}(\tilde{K}) = (E\underline{\tilde{I}} - \underline{\tilde{H}}^{\,C})^{-P_{c^*}}$ is the inverse in the subspace c^* complement of c, and $\tilde{H}^{\,C} = \underline{P}_C \underline{\tilde{H}} \underline{P}_C + \underline{S}(\tilde{K})$.

The matrix elements in the subspaces C and C^* are shown in the Appendix for a two-site CPA $(n = 2)$. The self-energy having been calculated, the Green functions are obtained from the Hilbert transform from the pure-host density of states $n(E)$.

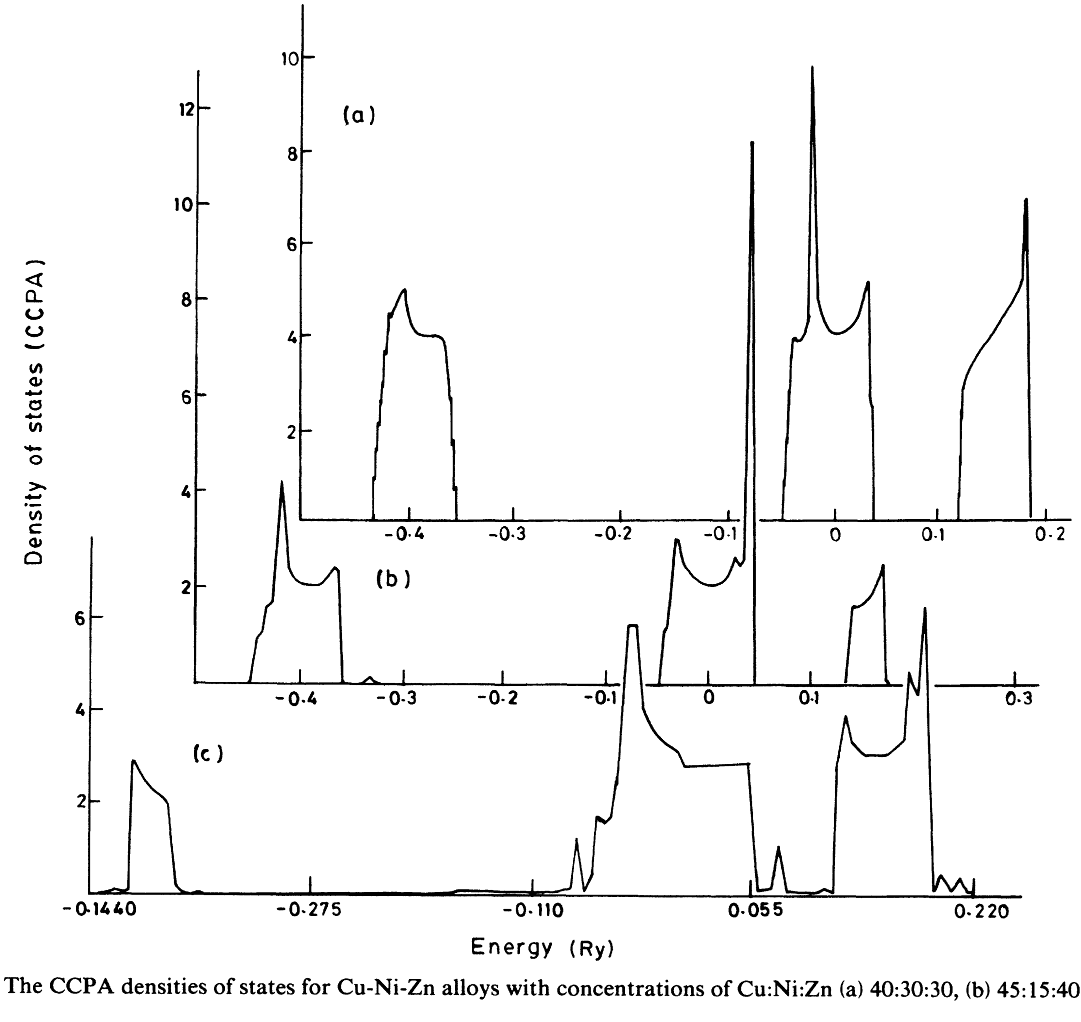

FIG. 1. The CCPA densities of states for Cu-Ni-Zn alloys with concentrations of Cu:Ni:Zn (a) 40:30:30, (b) 45:15:40, (c) 50:40:10.

III. RESULTS AND DISCUSSION

Figure 1 shows the two-site CCPA density of states for three different compositions of the ternary alloy of Cu-Ni-Zn. These are compared with the corresponding results in the single-site CPA (Fig. 2). It is well known that the configuration fluctuations arising out of random clustering, short-ranged order, and off-diagonal disorder may lead to additional structures which are suppressed in the single-site CPA. In a previous communication[18] on binary alloys we have argued that the dominant disorder-induced structures have their origin in the bonding-antibonding nature of states within the cluster. Figure 1 shows that a similar effect also is present in ternary alloys. Structures appear in the impurity bands on both sides of the central host Cu band. The impurity bands have two sharp peaks and these grow at the expense of the host as we increase the concentration of the impurities. The structure on the Ni side of the band is qualitatively very similar to the case of binary Cu-Ni.[18] The Zn part of the band has almost comparable peaks with a rounded central dip and these structures grow as the concentration of Zn is increased. In comparison the CPA density of states in the impurity region is almost featureless. Such clustering structures also appear in computer simulations of alloys. Mills and Ratanaravaraksa[4] have reported fine structure in a calculation on a model Hamiltonian on a simple cubic lattice by incorporating multiple scattering from pairs of sites within the traveling-cluster approximation (TCA). This suggests that the origin of the fine structure in the density of states has a microscopic origin in the disorder-induced configuration fluctuations in the system. Such clusters play a crucial role in order-disorder phase transitions and the energetics of such transitions requires a careful study of the cluster-based structures in the density of states. The augmented space provides a systematic way of studying such effects.

APPENDIX

For a two-site ternary alloy, the augmented subspace C described in the text is of rank 8 and is spanned by the basis

$$xf_{00},\ xf_{01},\ xf_{0-1},\ xf_{10},\ xf_{11}\ ,$$

$$xf_{1-1},\ xf_{-10},\ xf_{-11},\ xf_{-1-1}\ ,$$

$$yf_{00},\ yf_{01},\ yf_{0-1},\ yf_{10},\ yf_{11}\ ,$$

$$yf_{1-1},\ yf_{-10},\ yf_{-11},\ yf_{-1-1}\ .$$

We shall label these states as 1 to 18.

The ternary distribution matrix $\underline{M}$ is tridiagonal, as discussed before, and its matrix elements are

$$a_1=D,\quad a_2=[Dx_B/(B-D)^2]-D\ ,\ a_3=Dx_B/(D^2-B)\ ;$$

$$b_1^2=B-D^2,\quad b_2^2=x_B+C(D-C)\ ;$$

$$D=x_A-x_C;\quad B=x_A+x_C;\quad C=Dx_B/(B-D^2)\ ,$$

a being the diagonal and b the off-diagonal elements.

The matrix elements of the augmented Hamiltonian $\underline{\tilde{H}}$ in the subspace C are given below:

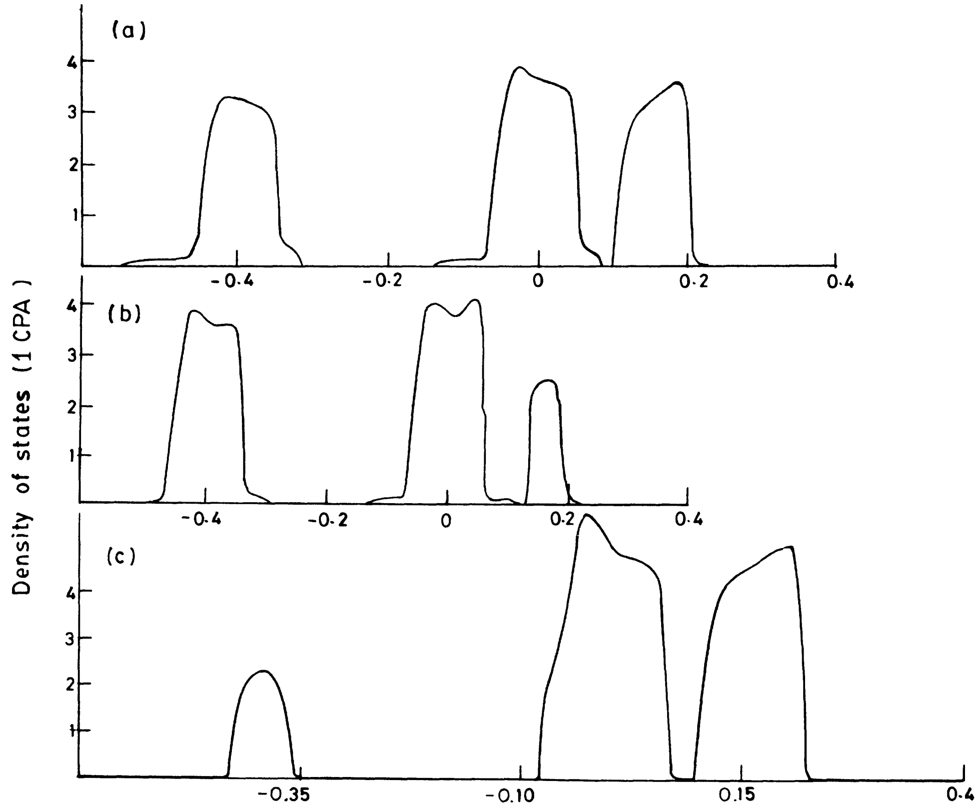

FIG. 2. The one-site CPA (1CPA) densities of states for Cu-Ni-Zn alloys with concentrations of Cu:Ni:Zn (a) 40:30:30, (b) 45:15:40, (c) 50:40:10.

$$\tilde{H}(1,1)=\tilde{H}(2,2)=e_1;\quad \tilde{H}(1,2)=\tilde{H}(2,1)=V\ ;$$

$$\tilde{H}(1,5)=\tilde{H}(2,11)=W_1;\quad \tilde{H}(1,8)=\tilde{H}(2,12)=D_2b_1b_2\ ;$$

$$\tilde{H}(3,3)=\tilde{H}(4,4)=\tilde{H}(13,13)=\tilde{H}(16,16)=e_1+S_0\ ;$$

$$\tilde{H}(5,5)=\tilde{H}(6,6)=\tilde{H}(7,7)=\tilde{H}(11,11)=\tilde{H}(14,14)=\tilde{H}(17,17)=e_2+S_0\ ;$$

$$\tilde{H}(8,8)=\tilde{H}(9,9)=\tilde{H}(10,10)=\tilde{H}(12,12)=\tilde{H}(15,15)=\tilde{H}(18,18)=e_3+S_0\ ;$$

$$\tilde{H}(3,6)=\tilde{H}(4,7)=\tilde{H}(13,14)=\tilde{H}(16,17)=W_1+S_1\ ;$$

$$\tilde{H}(3,9)=\tilde{H}(4,10)=\tilde{H}(13,15)=\tilde{H}(16,18)=D_2b_1b_2+S_1\ ;$$

$$\tilde{H}(5,7)=\tilde{H}(6,8)=\tilde{H}(7,9)=\tilde{H}(11,12)=\tilde{H}(14,15)=\tilde{H}(17,18)=W_2+S_1\ ;$$

$$e_1=e_B+D_1a_1+D_2(a_1^2+b_1^2)\ ;\quad e_2=e_B+a_2D_1+D_2(a_2^2+b_2^2+b_1^2)\ ;$$

$$e_3=e_B+a_3D_1+D_2(a_3+b_2)\ ;\quad W_1=D_1b_1+D_2(a_1+a_2)\ ;$$

$$W_2=D_1b_2+D_2b_2(a_2+a_3)\ ;\quad D_1=(e_A-e_C)/2;\quad D_2=(e_A+e_C-2e_B)/2\ ,$$

and $S_0(E)$ and $S_1(E)$ are the diagonal and off-diagonal elements of the surface potential which arises because the 18×18 cluster is immersed in the full self-consistent medium.

In case there is off-diagonal disorder, then, as discussed in the text there are six parameters in the expression for V_{ij}; these are given by

$$A=V_{BB};\quad B=(V_{AA}+V_{CC}-6V_{AB}-6V_{BC}+6V_{BB})/2\ ;$$

$$C=(V_{AB}+V_{BC}-2V_{BB})/2;\quad D=(V_{AB}+V_{BC}-V_{BB})\ ;$$

$$E=(6V_{AB}+6V_{BC}-4V_{BB}-V_{AA}-V_{CC})/2\ ;$$

$$F=(V_{BB}-V_{CC}+5V_{AB}+5V_{BC})\ .$$

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