Band calculation of the effect of magnetic impurity atoms on the properties of superconductors

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Magnetic impurity atoms scatter the conduction electrons of a host metal because of the exchange interaction. The phase shifts caused by this scattering are calculated from a crude model for conduction electrons with spin parallel or antiparallel to the spin of the impurity atom, for various alloy systems of interest (Cr, Mn, Fe, Co, and Ni in Al, Zn, Nb, In, Sn, Tl, and Pb). From the calculated phase shifts, the expected depression in the host metal's superconducting transition temperature is calculated, and the results are compared with experimental data. Partial waves beyond s waves are found to be essential; in fact, the p- and d-wave scattering dominate the s-wave scattering in many cases. The superconducting electronic density of states can also be calculated from the phase shifts, and good agreement with our results has been found with tunneling data obtained by Tsang and Ginsberg for In-Mn alloys.

I. INTRODUCTION

The partial or complete suppression of superconductivity by magnetic impurities from among the $3d$ elements of the Periodic Table is interesting because the exchange interaction, between the magnetic electrons of these impurity atoms and the conduction electrons of the host metal, is a strong one. A proper treatment of the interaction requires a theoretical analysis going beyond the classical perturbation treatment of Abrikosov and Gorkov.[1] This theoretical analysis has been supplied by two theories, that of Shiba,[2,3] also developed by Rusinov,[4] and that of Müller-Hartmann and Zittartz (MHZ).[5] Experimental results have usually been compared with the Shiba theory rather than with that of MHZ. There are two reasons for this. First, calculations by Nagi and co-workers[6–8] and others[9–13] derive both thermodynamic and transport properties according to the Shiba theory,[2] but no transport results have been derived from the MHZ theory. Second, in the equations of the Shiba theory, the spin S of the impurity atom always appears multiplied by the exchange constant J, so that there is in effect only one adjustable parameter, which is called ϵ_0 and is given by

$$\epsilon_0 = |(1-\zeta^2)/(1+\zeta^2)| \ , \tag{1}$$

where

$$\zeta = \tfrac{1}{2}\pi JSN_0 \tag{2}$$

and N_0 is the electron density of states for one spin direction at the Fermi surface in the normal state. We are speaking here of the method of applying Shiba's theory which has always been used, in which one assumes that only s-wave scattering of the conduction electrons from an impurity atom need be considered. In terms of the phase shifts δ_0^+ and δ_0^- for spin up and down, respectively (i.e., parallel and antiparallel to the spin of the impurity atom), ϵ_0 is given by

$$\epsilon_0 = \cos(\delta_0^+ - \delta_0^-) \ . \tag{3}$$

It has been known for some time[14] that the observed shift in the transition temperature δT_c is too large in several alloy systems to be accounted for if one takes only s-wave scattering into account. We have made a first attempt to include higher partial waves, using calculated values for the phase shifts δ_l^+ and δ_l^- associated with the scattering of partial waves with orbital angular momentum quantum number l and spin up or down, respectively. The way in which the higher partial waves can be included in the theory was outlined by Rusinov.[4] One of us has included them, and has derived useful expressions from which thermodynamic and transport properties can be calculated.[15]

The transition temperature T_c of the superconductor with magnetic impurity atoms of concentration C_i is given in terms of the pure superconductor's transition temperature T_{c0}, zero-temperature order parameter Δ_{00} and density of states N_0 by the relation

$$\ln(T_c/T_{c0}) = \psi(\tfrac{1}{2}) - \psi(\tfrac{1}{2} + pT_{c0}/4\gamma T_c) \ , \tag{4}$$

where ψ is the digamma function,

$$p = \frac{C_i}{\pi N_0 \Delta_{00}} \sum_l (2l+1)(1-\epsilon_l^2) \ , \tag{5}$$

$$\epsilon_l = \cos(\delta_l^+ - \delta_l^-) \ , \tag{6}$$

and

$$\gamma = \pi k_B T_{c0}/\Delta_{00} \simeq 1.781 \ . \tag{7}$$

From Eq. (4), one can show that if $|\delta T_c| \lesssim \frac{1}{2} T_{c0}$, then

$$\frac{\delta T_c}{C_i} \cong \frac{dT_c}{dC_i} = \frac{-1}{8N_0 k_B} \sum_l (2l+1)(1-\epsilon_l^2) \quad . \quad (8)$$

Throughout this paper, dT_c/dC_i is evaluated at $C_i = 0$. We have calculated phase shifts to obtain values of ϵ_l, and have used them with Eq. (8) to determine theoretical values of $\delta T_c/C_i$. We compare these values with those which have been experimentally observed. We take N_0 for each host metal from specific-heat data in the literature.[16]

It should be emphasized that the Shiba theory[2] on which our work is based assumes that the impurity atom's spin has a lifetime which is effectively infinite, and that the spin is treated classically to all orders of the exchange interaction. In actual samples, the presence of a localized magnetic moment on an impurity atom may depend on the crystallographic state of the host metal. For example, manganese atoms in indium have a magnetic moment in thin films,[17–19] but not in bulk samples.[20,21] It is also assumed that the entire effect of the impurity atom is due to its spin and the exchange interaction.

II. METHOD OF CALCULATION

In this study a large series of non-self-consistent calculations have been performed. The basic approximation to the exchange correlation potential is to assume the Kohn-Sham-Gaspar (KSG) form[22] in the spin-density limit. That is, one has a local exchange potential which depends upon local density of + spin electrons for + spin properties and upon − spin densities for − spin properties. The potential is further modified into the normal form of a muffin-tin potential.[23] In obtaining the muffin-tin potential we proceed as follows. For each host system (Al, Zn, Nb, In, Sn, Tl, or Pb), we determine a potential for the host atom in the KSG approximation in free space. In the region from a given host nucleus to the midpoint of the nearest-neighbor distance this potential is used. In the region between these tangent spheres, the average potential in this region is used as the constant potential. The next stage is to compute an approximate linear combination of atomic orbitals (LCAO) energy band[24] for this material in order to locate the Fermi energy with respect to the value for the average potential in the interatomic region. This serves to define our energy scale. We note that in the final analysis details of the superconducting behavior are weakly dependent upon the value of the Fermi energy, and thus its exact determination is for our purposes of little consequence.

The next stage is to incorporate the potential due to the impurity atom into the host. In performing this there are several initial difficulties. The first difficulty is to determine the exact atomic configuration of the impurity in the host. The impurities we consider are Cr, Mn, Fe, Co, and Ni. In free space these have a ground-state configuration of an Ar atom core plus $3d^n4s^2$ except for Cr which is $3d^54s$. In all cases the atoms have a ground state consistent with the above configuration in which spin magnetism is maximized. In the solid this need not be the case; spin quenchings and/or promotion of electrons may easily occur. In this study we therefore perform our calculations for several possible choices of atomic configuration. In general the results demonstrate substantial sensitivity to atomic configuration. We compute the spin-dependent potential for each state of each impurity atom in the KSG limit.

The next stage is to incorporate this potential into the host lattice. We are unable to determine by our calculation or from experiment the amount of relaxation of the positions of the lattice ions around the impurity or the exact effects of electron charge transfer to or from the impurity. Thus the impurity potential is assumed to simply replace a host potential. At this level of approximation, this introduced a large discontinuity in the potential at the radius of the impurity muffin tin. This discontinuity is physically unreasonable, and we find that for energies near the Fermi energy the effect of the discontinuity dominates the impurity phase shift and almost eliminates the spin dependence. We correct for this, and our neglect of charge exchange, and/or lattice relaxation by ansatz: We simply adjust this impurity potential by a constant value so that it smoothly joins the host-lattice potential. In the limit of low-impurity concentration, which is of interest here, this seems to be a reasonable ansatz, that the host acts as a source or sink of charge to permit the impurity to equilibrate with the lattice while the lattice remains unchanged.

The final step in the calculation is to integrate the radial Schrödinger equation inside the impurity muffin tin from the origin outward and determine the phase shifts at the muffin-tin boundary. In doing this we use the Runge-Kutta[25] method of integrating the Schrödinger equation and from this solution, determine the phase shifts by standard means.[26] Partial waves of $l = 0, 1, 2, 3$ are considered. We find for this study only $l = 0, 1, 2$ are necessary. In fact on average each of these three contributions is of roughly equal value, contradicting the usual assumption that only s-wave scattering need be included. We believe that the neglect of the actual host-lattice charge density inside the impurity atom's muffin tin is not a serious neglect here, since this would be spin independent, and what we need is only the *difference* between the phase shifts for the + and − spin. We tested our phase-shift program on several known cases, including square wells and Al and Cu potentials, for which the phase shifts are available in the literature[27]; the computed phase shifts agree well with

the known values.

It has not been possible to adjust the radius of the impurity ion's muffin-tin sphere to judge the sensitivity of our results to this parameter because such an adjustment would imply a lattice relaxation if the muffin tins are to be kept tangent. This adjustment is therefore beyond the scope of our present calculation. However the sensitivity of our results to a constant change of the impurity potential with respect to the Fermi energy was studied. This is equivalent here to studying the effect of making different choices of Fermi energy and/or using different values of the constant potential outside the muffin-tin radius. In general, the phase shifts were sensitive to this, varying by 20% or so over a change in potential of ±1.5 eV. However the relevant physics is in the *difference* of phase shifts $(\delta_l^+ - \delta_l^-)$, as seen in Eqs. (4)–(8), and we found this difference to be altered by only 2% or so for such a change. Hence, the values of $\delta T_c/C_i$ and other experimentally relevant parameters are insensitive to the impurity potential. Nonetheless, in future work it would be desirable to eliminate the ambiguities which arise from the use of a muffin-tin potential.

These calculations were performed in a few hours by a Digital Equipment Corporation LSI-11 microcomputer.

III. RESULTS OF THE CALCULATION

Calculations were performed for impurities of Cr, Mn, Fe, Co and Ni, each in several possible atomic configurations, in the host metals Al, Zn, Nb, In, Sn, Tl, and Pb. We note here that not all these magnetic atoms remain magnetic in all of these hosts. For example in the case of bulk samples of Al, these impurities are not magnetic.[28] None the less we performed the calculations for all possible cases, since a local moment may be present in a different crystallographic phase of the host metal. In addition, the phase shifts, δ_l, were calculated for both + and − spin electrons for $l = 0, 1, 2, 3$. In all cases we found that at the Fermi energy δ_3 is small compared to the others and that $\delta_3^+ - \delta_3^-$ is even smaller compared to the differences of the other δ_l's. Please note that the effect of the magnetic impurity on the transition temperature is dependent only on the difference $(\delta_l^+ - \delta_l^-)$. We found for various hosts and a given impurity that the magnitude of δ_l varies substantially from host to host, while the value of the difference $(\delta_l^+ - \delta_l^-)$ is usually much more constant within a given atomic configuration of the impurity. We also looked at δ_l's over an appreciable energy range about the host Fermi energy and found that $(\delta_l^+ - \delta_l^-)$ is quite insensitive to the exact Fermi energy.

In Table I, we show all phase shifts computed for

TABLE I. The phase shifts, δ_l, with $l = 0, 1, 2, 3$ for + and − spin of Cr at the Fermi energy are given for several hosts. The method of determination is given in the text. The phase shifts are in radians.

		$l=0$		$l=1$		$l=2$		$l=3$	
Cr state	Host	+	−	+	−	+	−	+	−
$3d^5 4s$, spin maximum (No. 1)	Al	0.8223	0.3283	1.2957	0.5118	0.0567	−0.0665	−0.0198	−0.0245
	Zn	0.7335	0.2200	1.0372	0.3905	0.0137	−0.0776	−0.0213	−0.0244
	Nb	0.6113	0.1769	1.2128	0.4932	0.1154	−0.0721	0.0024	−0.0118
	In	0.7188	0.2551	1.2578	0.5037	0.0813	−0.0702	−0.0115	−0.0199
	Sn	0.6909	0.2350	1.2467	0.5012	0.0893	−0.0709	−0.0085	−0.0181
	Tl	1.5505	0.9647	−1.0284	0.6215	0.0598	−0.0231	−0.0261	−0.0263
	Pb	1.1548	0.6341	−1.3560	0.5892	0.1145	−0.0388	−0.0185	−0.0241
$3d^5$, all + spin; $4s$, $1-$ spin (No. 2)	Al	0.7818	0.5344	1.1749	0.8136	0.0409	−0.0533	−0.0210	−0.0222
	Zn	0.6944	0.3945	0.9434	0.5680	0.0074	−0.0722	−0.0219	−0.0232
	Nb	0.5766	0.3458	1.1142	0.7794	0.0863	−0.0453	−0.0012	−0.0050
	In	0.6812	0.4422	1.1482	0.7995	0.0598	−0.0514	−0.0136	−0.0158
	Sn	0.6541	0.4173	1.1400	0.7948	0.0660	−0.0503	−0.0109	−0.0134
	Tl	1.5008	1.3386	−1.3159	−1.5196	0.0342	−0.0072	−0.0262	−0.0262
	Pb	1.1094	0.9190	−1.5582	1.2954	0.0726	−0.0095	−0.0206	−0.0203

Cr in several hosts. This table illustrates the smallness of δ_3 so in all further tables we do not list values of δ_3. The atomic configurations chosen for Cr are the atomic ground state $3d^5 4s$ where all unpaired spins are parallel and a $3d^5 4s$ configuration in which the $4s$ spin opposes those of the $3d^5$ electrons. In Table II, the computed phase shifts for Mn are given. The atomic states studied are $3d^5 4s^2$ with spin maximum; $3d^6 4s$, spin maximum; $3d^6 4s$ with the $4s$ spin opposing the maximum net spin of the $3d$ electrons; and $3d^7$ with spin maximum. In Table III, the phase shifts for Fe are shown. Fe is treated in the atomic ground state $3d^6 4s^2$, spin maximum; $3d^7 4s$, spin maximum; $3d^7 4s$ with the $4s$ spin opposing the maximum spin of the $3d$ shell; and in the state $3d^8$, spin maximum. In Table IV, the phase shifts for Co in various hosts are given. Co is considered in the atomic ground-state configuration $3d^7 4s^2$, spin maximum; $3d^8 4s$, spin maximum; $3d^8 4s$ with the s spin opposing that of the spin-maximum d shell. Finally, in Table V, the phase shifts for Ni impurities are given. Ni is computed in the atomic ground state $3d^8 4s^2$, spin maximum; $3d^9 4s$, spin maximum, and $3d^9 4s$ with the s spin opposing that of the spin-maximum d shell.

Using these phase shifts, Eq. (8) is used to compute the effect of impurity concentration on superconducting transition temperature for each atomic configuration for each impurity in each host. All these results, along with available experimental numbers are shown in Table VI. It may be seen that in most cases there exists one and only one atomic configuration of the impurity in a given host for

TABLE II. The phase shifts, δ_l, with $l = 0, 1, 2$, for + and − spin of Mn at the Fermi energy are given for several hosts. The method of determination is outlined in the text. The phase shifts are in radians.

Mn state	Host	$l=0$ +	$l=0$ −	$l=1$ +	$l=1$ −	$l=2$ +	$l=2$ −
$3d^5$,	Al	1.1450	0.9706	− 1.2268	− 1.5678	0.3343	0.1630
all +;	Zn	1.0983	0.9074	− 1.3330	1.3741	0.1909	0.0895
$4s^2$ (No.1)	Nb	0.9354	0.7596	− 1.3810	1.4581	0.6090	0.2931
	In	1.0423	0.8670	− 1.3014	1.5189	0.4562	0.2195
	Sn	1.0146	0.8392	− 1.3218	1.5035	0.4936	0.2371
	Tl	− 1.3138	− 1.4791	− 0.5765	− 0.8142	0.2127	0.1187
	Pb	1.4545	1.2811	− 0.8732	− 1.1306	0.4916	0.2459
$3d^6$,	Al	0.9201	0.6285	1.4674	0.8527	0.0983	− 0.0039
5+,	Zn	0.8496	0.5351	1.2444	0.6736	0.0446	− 0.0235
1−;	Nb	0.7087	0.4441	1.3647	0.8318	0.1838	0.0140
$4s$,	In	0.8164	0.5383	1.4193	0.8450	0.1348	0.0030
1+ (No. 2)	Sn	0.7885	0.5139	1.4056	0.8421	0.1464	0.0054
	Tl	− 1.5195	1.3319	− 0.8963	1.2025	0.0822	0.0107
	Pb	1.2364	0.9506	− 1.2168	1.1022	0.1630	0.0215
$3d^6$,	Al	0.8805	0.7464	1.3334	1.1333	0.0729	0.0184
5+,	Zn	0.8104	0.6466	1.1284	0.8720	0.0342	− 0.0141
1−;	Nb	0.6744	0.5430	1.2574	1.0731	0.1374	0.0556
$4s$,	In	0.7794	0.6467	1.2989	1.1068	0.1004	0.0335
1− (No. 3)	Sn	0.7521	0.6198	1.2887	1.0986	0.1091	0.0386
	Tl	− 1.5669	1.4883	− 1.1607	− 1.1673	0.0445	0.0397
	Pb	1.1928	1.0880	− 1.4120	− 1.5039	0.0988	0.0716
$3d^7$,	Al	0.5257	0.2821	0.7392	0.4829	− 0.1426	− 0.5939
spin maximum (No. 4)	Zn	0.4081	0.1532	0.5455	0.3435	− 0.1488	− 0.5509
	Nb	0.3453	0.1318	0.7160	0.4582	− 0.1452	− 0.4028
	In	0.4376	0.2094	0.7301	0.4718	− 0.1451	− 0.4659
	Sn	0.4138	0.1895	0.7269	0.4685	− 0.1454	− 0.4454
	Tl	1.2710	1.0065	1.1908	0.7621	− 0.1372	0.1012
	Pb	0.8753	0.6325	1.0361	0.6558	− 0.1268	0.8853

TABLE III. The phase shifts, δ_l, with $l=0, 1, 2$, for + and − spin of Fe in various hosts at the Fermi energy are given. The method of calculation is outlined in the text. The phase shifts are in radians.

Fe state	Host	$l=0$ +	$l=0$ −	$l=1$ +	$l=1$ −	$l=2$ +	$l=2$ −
$3d^64s^2$	Al	1.1471	1.0158	− 1.2691	− 1.5282	0.2688	0.1626
spin maximum (No. 1)	Zn	1.1014	0.9603	− 1.3769	1.4405	0.1618	0.0944
	Nb	0.9410	0.8082	− 1.4137	1.4987	0.4887	0.2916
	In	1.0460	0.9139	− 1.3389	1.5590	0.3652	0.2186
	Sn	1.0188	0.8865	− 1.3581	1.5437	0.3950	0.2360
	Tl	− 1.3226	− 1.4484	− 0.6249	− 0.8191	0.1483	0.1025
	Pb	1.4513	1.3187	− 0.9162	− 1.1203	0.3491	0.2217
$3d^74s$,	Al	0.9077	0.6763	1.3905	0.8843	0.0759	− 0.0007
spin maximum (No. 2)	Zn	0.8391	0.5940	1.1746	0.7177	0.0325	− 0.0193
	Nb	0.7011	0.4924	1.3044	0.8664	0.1444	0.0183
	In	0.8063	0.5862	1.3508	0.8781	0.1051	0.0067
	Sn	0.7790	0.5619	1.3393	0.8756	0.1143	0.0093
	Tl	− 1.5401	1.3581	− 1.0039	1.1666	0.0622	0.0096
	Pb	1.2194	0.9851	− 1.3089	1.1011	0.1242	0.0207
$3d^7$,	Al	0.8561	0.7836	1.2184	1.1549	0.0513	0.0206
5+,	Zn	0.7884	0.6964	1.0310	0.9161	0.0218	− 0.0098
2−;	Nb	0.6567	0.5825	1.1655	1.0980	0.0996	0.0580
$4s$,	In	0.7582	0.6849	1.1955	1.1300	0.0717	0.0359
1− (No. 3)	Sn	0.7319	0.6584	1.1883	1.1223	0.0783	0.0410
	Tl	1.5375	1.5026	− 1.4103	− 1.2175	0.0307	0.0350
	Pb	1.1614	1.1107	1.5540	− 1.5246	0.0690	0.0657
$3d^8$,	Al	0.4704	0.3130	0.6437	0.4919	− 0.2697	− 1.1804
spin maximum (No. 4)	Zn	0.3611	0.1985	0.4860	0.3648	− 0.2607	− 1.0484
	Nb	0.3024	0.1646	0.6263	0.4704	− 0.2391	− 0.5359
	In	0.3886	0.2412	0.6368	0.4824	− 0.2517	− 0.7149
	Sn	0.3663	0.2215	0.6344	0.4795	− 0.2481	− 0.6525
	Tl	1.1797	0.9947	0.9300	0.7035	0.2019	0.0683
	Pb	0.8024	0.6394	0.8411	0.6248	− 0.4736	0.3646

which dT_c/dC_i as computed agrees well with the experiment. One exception to this rule is Mn in Zn, for which no studied configuration has a large enough effect. The other exception is Mn in Pb, for which the experimental value lies between two theoretical possibilities. In this case it is possible that several Mn configurations coexist in the host or a configuration not tried here is the correct one.

Recently, a tunneling measurement was made on the system Mn in In by Tsang and Ginsberg.[29] A consequence[15] of Shiba's theory is that the magnetic impurities introduce a band of local excited states for each $\epsilon_l \neq 1$, with energy around $\epsilon_l\Delta$ where Δ is the superconducting order parameter (not the gap parameter). Experimentally,[14] $-dT_c/dC_i$ is found to be 51, and if Mn is in the state $3d^64s$, spin maximum, the theory predicts that $-dT_c/dC_i = 43.9$. Using the phase shifts determined for that configuration by our calculation, Tsang and Ginsberg computed the energy of the impurity states and the number of those states, and found excellent agreement with their experiment. (The phase shifts determined for the other three configurations do not agree with the tunneling data at all.) Their results demonstrate the necessity of including higher order phase shifts, rather than only the one for $l=0$.

Levin *et al.*[30] have made tunneling measurements on samples in which Mn was ion-implanted in Pb and Sn. They state that their results indicate a band of states with $\epsilon_l = 0.70$ in each case. This result is compatible with our calculated value $\epsilon_1 = 0.68$ in Pb-Mn (configuration No. 2), for which, however, their

TABLE IV. The phase shifts, δ_l, with $l=0, 1, 2$ and + and − spin of Co in various hosts at the Fermi energy are given. The method of calculation is outlined in the text. The phase shifts are in radians.

Co state	Host	$l=0$ +	$l=0$ −	$l=1$ +	$l=1$ −	$l=2$ +	$l=2$ −
$3d^74s^2$,	Al	1.2230	1.1395	− 1.1611	− 1.3129	0.3345	0.2392
spin maximum (No. 1)	Zn	1.1796	1.0940	− 1.2421	− 1.4297	0.2020	0.1443
	Nb	1.0224	0.9358	− 1.3123	− 1.4502	0.6095	0.4317
	In	1.1246	1.0395	− 1.2343	− 1.3790	0.4565	0.3234
	Sn	1.0981	1.0126	− 1.2543	− 1.3973	0.4939	0.3495
	Tl	− 1.2450	− 1.3355	− 0.5482	− 0.6609	0.1841	0.1410
	Pb	1.5320	1.4403	− 0.8336	− 0.9527	0.4422	0.3186
$3d^84s$,	Al	0.9929	0.8507	1.5357	1.1544	0.1127	0.0455
spin maximum (No. 2)	Zn	0.9358	0.7863	1.3503	0.9821	0.0599	0.0199
	Nb	0.7872	0.6567	1.4332	1.1159	0.2054	0.0884
	In	0.8919	0.7554	1.4875	1.1386	0.1526	0.0637
	Sn	0.8648	0.7298	1.4738	1.1333	0.1652	0.0695
	Tl	− 1.4727	1.5191	− 0.8867	− 1.5630	0.0804	0.0269
	Pb	1.2950	1.1488	− 1.1881	1.4464	0.1652	0.0601
$3d^8$,	Al	0.9454	0.9247	1.3590	1.3999	0.0777	0.0783
5+,	Zn	0.8884	0.8595	1.1909	1.1889	0.0443	0.0348
3−;	Nb	0.7458	0.7203	1.2926	1.3152	0.1420	0.1478
4s,	In	0.8474	0.8243	1.3293	1.3609	0.1053	0.1080
1− (No. 3)	Sn	0.8210	0.7973	1.3203	1.3495	0.1140	0.1174
	Tl	− 1.5313	− 1.5307	− 1.2449	− 0.9952	0.0389	0.0648
	Pb	1.2416	1.2320	− 1.4438	− 1.3013	0.0899	0.1282

TABLE V. The phase shifts, δ_l, with $l=0, 1, 2$ for + and − spin of Ni in various hosts at the Fermi energy are given. The method of calculation is given in the text. The phase shifts are in radians.

Ni state	Host	$l=0$ +	$l=0$ −	$l=1$ +	$l=1$ −	$l=2$ +	$l=2$ −
$3d^8$	Al	1.2178	1.1633	− 1.2144	− 1.3153	0.2639	0.2175
$4s^2$	Zn	1.1750	1.1195	− 1.3006	− 1.4237	0.1666	0.1363
spin maximum (No. 1)	Nb	1.0199	0.9634	− 1.3558	− 1.4467	0.4791	0.3915
	In	1.1206	1.0652	− 1.2828	− 1.3785	0.3581	0.2434
	Sn	1.0945	1.0388	− 1.3015	− 1.3960	0.3873	0.3169
	Tl	− 1.2630	− 1.3208	− 0.6049	− 0.6837	0.1314	0.1146
	Pb	1.5200	1.4606	− 0.8851	− 0.9665	0.3161	0.2656
$3d^94s$,	Al	0.9795	0.8699	1.4597	1.1347	0.0885	0.0408
spin maximum (No. 2)	Zn	0.9229	0.8106	1.2741	0.9786	0.0453	0.0183
	Nb	0.7777	0.6796	1.3729	1.1049	0.1632	0.0798
	In	0.8803	0.7764	1.4195	1.1232	0.1206	0.0574
	Sn	0.8537	0.7513	1.4079	1.1191	0.1306	0.0626
	Tl	− 1.4930	1.5234	− 0.9867	1.4573	0.0627	0.0223
	Pb	1.2777	1.1600	− 1.2738	1.3794	0.1290	0.0513
$3d^9$,	Al	0.9172	0.9463	1.2332	1.3947	0.0552	0.0729
5+,	Zn	0.8611	0.8861	1.0766	1.1985	0.0296	0.0334
4−;	Nb	0.7239	0.7452	1.1912	1.3163	0.1031	0.1378
4s,	In	0.8222	0.8475	1.2157	1.3588	0.0756	0.1006
1− (No. 3)	Sn	0.7967	0.8209	1.2099	1.3483	0.0821	0.1093
	Tl	1.5705	− 1.5215	− 1.5203	− 1.0434	0.0273	0.0561
	Pb	1.2071	1.2468	1.5081	− 1.3308	0.0637	0.1133

TABLE VI. The rate of depression of transition temperature with impurity concentration, $-dT_c/dC_i$, in ° K/at.%, are given for various hosts and impurities. The theoretical numbers are given for several possible atomic state of the impurity. Experimental numbers are given, where available. The state Nos. refer to the atomic configurations which are given in the previous five tables. The experimental values are taken from publications which are listed in Ref. 14.

Impurity \ Host	Al	Zn	Nb	In	Sn	Tl	Pb
Cr No. 1	90.6	143	14.5	72.2	66.1	155.0	67.5
Cr No. 2	24.2	54.5	4.06	19.6	18.1	7.32	7.10
Cr Expt.				65	16		
Mn No. 1	25.8	64.6	6.85	25.4	25.0	11.0	11.9
Mn No. 2	57.2	104.0	8.66	43.9	40.0	109.0	40.8
Mn No. 3	7.63	24.1	1.33	6.26	5.80	0.358	0.910
Mn No. 4	60.7	99.2	4.96	31.2	26.5	40.3	92.7
Mn Expt.		295		51			21
Fe No. 1	13.6	36.2	3.20	12.5	12.1	6.42	5.05
Fe No. 2	39.7	68.5	5.81	30.1	27.3	98.5	33.0
Fe No. 3	1.11	5.52	0.244	1.03	0.987	5.19	0.331
Fe No. 4	162	270	4.56	45.8	33.7	12.7	66.7
Fe Expt.				2.25	1.1		4.7
Co. No. 1	6.10	13.4	1.94	6.62	6.68	2.58	2.89
Co. No. 2	23.1	43.7	3.31	17.1	15.5	56.4	17.9
Co. No. 3	0.275	0.135	0.0213	0.151	0.125	8.68	1.55
Co Expt.				0.07	0.15		0.8
Ni No. 1	2.23	5.52	0.581	2.16	2.12	1.09	0.823
Ni No. 2	16.6	28.3	2.24	12.0	10.8	58.7	16.1
Ni No. 3	4.04	4.70	0.468	2.72	2.39	29.7	6.39
Ni Expt.							

value $-dT_c/dC_i = 16$ K/at.% is in only fair agreement with the calculated value of 40.8 K/at.%. In the case of Sn-Mn, their value $-dT_c/dC_i = 14$ K/at.% indicates that we should examine configurations No. 1 and No. 3 (see Table VI). However, all the calculated ϵ_l values for those configurations are 0.95 or larger, so the agreement between theory and their results for Sn-Mn is poor. It is difficult to assess the significance of the work of Levin *et al.*, because the impurity concentrations in their samples were known to be inhomogeneous. Furthermore, these investigators have apparently estimated ϵ_0 by setting the energy about which the impurity band forms equal to ϵ_0 times the gap energy, rather than ϵ_0 times Δ. When a pair-breaking interaction[31] such as the exchange interaction is present, the gap energy is not equal to Δ, and Δ can therefore not be obtained directly by an examination of the tunneling curve.

Finally, the authors wish to caution the reader. The phase-shift calculations reported here have been made for a host metal, not for a free-electron gas, and thus the phase shifts given in Tables I–V are not expected to satisfy the Friedel sum rule. We do note, however, that if one subtracts the phase shift at the Fermi energy for a host atom from those in Tables I–V, the Friedel sum rule is approximately satisfied here as well.

IV. CONCLUSIONS

We have developed a crude model for magnetic impurities in a superconducting host. This model is appropriate for low-impurity concentrations so that the neglect of impurity-impurity interaction is valid.[32] We have found that, despite its crudeness, the model is capable of predicting dT_c/dC_i with some quantitative accuracy for a variety of examples. Furthermore, these calculations are sufficiently sound to conclusively demonstrate several points. These are: (i) partial waves beyond $l = 0$ are essential to obtain quantitatively accurate descriptions. In fact in many cases δ_1 and/or δ_2 are the dominant ones. (ii) For the examples studied, δ_3 is not important. (iii) In all cases the atomic state of the impurity in the host has

a large effect upon the computed value of dT_c/dC_i. (iv) A given impurity may not have the same atomic configuration in all hosts.

Despite the apparent quantitative success of this model for a variety of systems, there is much work to be done to make the theoretical situation fully satisfactory. One might try various choices of exchange correlation potentials on the phase shifts to determine the effect of these on dT_c/dC_i. One might try to study the effect of lattice relaxation around the impurity. However, due to the nonmagnetic nature of the host this is likely to have little direct effect upon dT_c/dC_i. Probably the most important advance would be to self-consistently compute the charge and spin densities of the impurity in the host while calculating the total energy so that one might predict which "atomic" configuration a given impurity takes on in a given host. Of course, one can then use self-consistently determined charge and spin densities to determine the impurity potential and compute the phase shifts from them. It would be desirable to eliminate the muffin-tin potential, but this definitely complicates the calculation, and we believe the muffin-tin potential is not a very severe approximation in these cases.

Our theoretical results are in good agreement with experimental tunneling data for In-Mn alloys, but are in only fair agreement for Pb-Mn, and poor agreement for Sn-Mn. In the latter two cases, the samples were produced by ion bombardment, which is known to yield inhomogeneous samples. The experiments on Pb-Mn and Sn-Mn alloys should be performed on homogeneous samples to try to cast further light on the fundamental properties of those alloys.

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