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Hyperfine Fields and Curie Temperatures of the Heusler Alloys Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn†

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The effective magnetic fields at all non-Mn sites, the nuclear-hyperfine contributions to the specific heat, and the paramagnetic Curie temperatures have been calculated for the Heusler alloys Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn, by an extension of the virtual-bound-state (resonance) model previously used by Caroli and Blandin. The required electronic ξ factors are determined from paramagnetic-susceptibility and Knight-shift data on dilute Cu-base binary alloys; and a phenomenological procedure is used to estimate the reduction in ξ factors appropriate for the corresponding ions in the Heusler alloys. The latter effect is important, and failure to take the reduced s-wave character into account yields hyperfine fields which are too large by a factor of 2–4 for the polyvalent ions. Our predictions for those saturation hyperfine fields which have not yet been determined are -355 ± 45 KOe for In in Cu_2MnIn, and -280 ± 45 and -260 ± 100 kOe for Cu and Sn, respectively, in Cu_2MnSn. The nuclear-hyperfine contribution to the specific heat of Cu_2MnIn is predicted to be $(5.94\pm1.11\ \mathrm{mJ\,{}^\circ K\ mole^{-1}})/T^2$. We give a critical and comprehensive comparison of theoretical results and available experimental data.

I. INTRODUCTION

THE Heusler[1–3] alloys of type Cu_2MnX, where X is Al, In, or Sn, are strongly ferromagnetic although none of the components are ferromagnetic. The electronic structure plays a significant role in determining the magnetic properties of these alloys and there has been a good deal of recent experimental work which has been helpful in clarifying this role. The crystal structure and spontaneous magnetization of Cu_2MnAl, CuMnIn, and CuMnSn are established.[1–7] Extensive neutron-diffraction studies[7–9] have been carried out on Cu_2MnAl with the conclusion that the magnetic moment per "molecule," which is of order $4\mu_B$, is concentrated on the Mn ion to within $0.1\mu_B$. The magnetic hyperfine field strengths at the Mn and Cu sites in Cu_2MnAl and Cu_2MnIn have been determined by NMR and found to be of order 200 kOe.[10,11] The Al field strength in Cu_2MnAl has similarly been determined by NMR to be about 68 kOe,[11] although a nuclear specific-heat study (on a slightly nonstoichiometric sample) yielded 158 kOe.[12] The hyperfine field strength at Sn sites in Cu_2MnSn was studied by Mössbauer techniques[13,14] but the results are contradictory. The low-temperature specific heats of Cu_2MnAl and Cu_2MnSn have been measured[12] and the nuclear hyperfine contributions have been analyzed. In Table I, we summarize some crystallographic and magnetic data which are pertinent to our paper.

On the theoretical side, Caroli and Blandin[15] have used the virtual-bound-state model[16,17] to estimate the hyperfine fields H_{eff} at the Cu sites in Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn and at the Al site in Cu_2MnAl, and have also calculated the paramagnetic Curie temperatures T_c of these alloys by using the double-resonance model of Caroli[18] to estimate the magnetic energy of interaction of a pair of Mn ions. These calculations are semiphenomenological, as experimental data are used to determine parameters of the theory. In view of the interest of Heusler alloys in the study of the role of electronic structure in concentrated magnetic alloys, we have attempted to refine some computational points of Caroli and Blandin's model and to extend it to calculate the effective fields at In and Sn sites in Cu_2MnIn and Cu_2MnSn, respectively. We have considered the following points.

The determination of H_{eff} and T_c requires sums over selected lattice sites of long-range oscillatory functions. The convergence of such sums is not rapid, in general. In the case of T_c, the convergence can be so slow that not even the correct sign is obtained by restricting the sums to the first few (four or five) nearest-neighbor shells. In such cases, an additional effect, due to imperfect ordering, is significant.

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TABLE I. Selected experimental data on Heusler alloys. $2a_L$, lattice constant (Å); M, saturation magnetic moment per Mn ion (μ_B); θ_f, ferromagnetic Curie temperature (°K); A, constant in the A/T^2 nuclear-hyperfine contribution to specific heat (mJ °K/mole); H (Cu), saturation hyperfine field strength at Cu sites (kOe); H (X), saturation hyperfine field strength at X=Al, In, or Sn sites (kOe).

	$2a_L$	M	θ_f	A	H (Cu)	H (X)
Cu_2MnAl	5.949[a]	4.12[a]	630[a]	1.89 ± 0.04[b]	212.5[c]	
					212.6[d]	68.2[d]
		3.60 ± 0.04[e]				
Cu_2MnIn	6.206[a]	3.95[a]	500[a]	···	197.3[c]	···
Cu_2MnSn	6.173[a]	4.11[a]	···	3.10 ± 0.14[b]	···	76[f]
						200 ± 35[g]

[a] Reference 5.
[b] Reference 12.
[c] Reference 10.
[d] Reference 11.
[e] Reference 6.
[f] Reference 13.
[g] Reference 14.

To calculate H_{eff} at a given site, one requires the amplitude squared of the Fermi-electron Bloch functions $|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}$, at the site in question. This information is obtained from Knight-shift data for the corresponding ion and from the paramagnetic susceptibility, χ_p. Caroli and Blandin used the data compiled by Knight[19] which were based on the assumption that χ_p is simply proportional to the electronic specific heat. We have used the more accurate recent calculations of χ_p by Bennett, Mebs, and Watson,[20] and Knight-shift data for solute ions in dilute Cu-base binary alloys to define a set of Bloch enhancement factors for the relevant ions in the simple electronic environment of pure Cu. Relative to this base line, estimates are then given for the reduction, due to smaller s-wave components, in enhancement factors for ions in the Heusler alloys. This reduced s-wave character is particularly important for the polyvalent ions. Without this correction, hyperfine fields can be overestimated by as much as a factor of 4.

There is not yet complete agreement on the value of the magnetic moment per molecule to be associated with these Heusler alloys. For example, in the case of Cu_2MnAl, Oxley, Tebble, and Williams[5] quote a saturation moment (in units of the Bohr magneton) of 4.12 (which was used by Caroli and Blandin), while a subsequent study by Endô, Ohoyama, and Kimura[6] yielded 3.60±0.04. Furthermore, extrapolation of the 77°K data of Felcher, Cable, and Wilkinson[8] and of Takata[9] by means of the $T^{3/2}$ law yields saturation moments of 3.75 and 3.65, respectively. As it was Sugibuchi and Endô[10] and Ogawa and Smit[11] (using a sample provided by Cable) who took the NMR data with which calculated results are to be compared, we have studied extensively the sensitivity of our results to the assumed value of the magnetic moment per Mn ion, which is an important parameter of the theory.

The calculations of hyperfine fields, using the dilute alloy enhancement factors, and Curie temperatures are given in Secs. II and III, respectively. The determination of a set of enhancement factors, which are consistent with the available experimental data, is discussed in Sec. IV and the predictions of the analysis are discussed. Section V consists of a summary.

II. HYPERFINE FIELDS IN BINARY-ALLOY APPROXIMATION

The hyperfine fields at the Mn sites cannot be obtained theoretically without detailed calculation of the electronic wave functions within the Mn ion core. However, the fact that the hyperfine fields at the Cu and Al sites are of the same magnitude as those at the Mn sites[10,11] suggests that the former may be accounted for by the coupling, via the Fermi contact interaction, of the spin polarization induced in the conduction band, by the Mn ion spin splitting, with the nuclear magnetic moments at the "nonmagnetic" ion sites. The effective magnetic field at such a lattice site $\mathbf{R}_0$ is then given by

$$H_{\text{eff}}(\mathbf{R}_0)=(8\pi/3)\mu_B P(\mathbf{R}_0)\,, \tag{1}$$

where $P(\mathbf{R}_0)$ is the total spin polarization at $\mathbf{R}_0$. Even in fields of order 200 kOe, the total spin polarization at non-Mn sites is still small enough to consider it as the sum of individual contributions, one from each Mn ion (at the lattice point $\mathbf{R}_n$),

$$P(\mathbf{R}_0)=\sum_n \rho(\mathbf{R}_{n0})\,, \tag{2}$$

where $\mathbf{R}_{n0}=\mathbf{R}_n-\mathbf{R}_0$. The calculation of $P(\mathbf{R}_0)$ is, thus, reduced to a one-impurity problem. For the spin polarization $\rho(\mathbf{R}_{n0})$, induced at $\mathbf{R}_0$ by the Mn ion at $\mathbf{R}_n$, Caroli and Blandin used

$$\rho(\mathbf{R}_{n0})=\Omega_0|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}\rho_0(\mathbf{R}_{n0})\,, \tag{3}$$

where Ω_0 is the average volume per ion, $|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}$ is the square of the Fermi-surface average of the amplitude of the Bloch electron wave functions at the site $\mathbf{R}_0$, and $\rho_0(\mathbf{R}_{n0})$ is the spin polarization for the corresponding Mn ion in a free-electron gas. Following the now traditional arguments,[16,17] the latter is given by the d-wave component in a partial wave expansion of the electron wave functions about the Mn sites and Caroli and Blandin used its well-known asymptotic form (valid for $k_F R_{n0}\gg1$)

$$\rho_0(\mathbf{R}_{n0})\approx-(5/4\pi^2R_{n0}{}^3)[\sin\delta_d{}^{\uparrow}\cos(2k_FR_{n0}+\delta_d{}^{\uparrow}) -\sin\delta_d{}^{\downarrow}\cos(2k_FR_{n0}+\delta_d{}^{\downarrow})]\,. \tag{4}$$

The d-wave phase shift for electrons of spin σ, $\delta_d{}^{\sigma}$ is given in terms of the corresponding screening charge $Z_d{}^{\sigma}$ by Friedel's[21] theorem

$$\delta_d{}^{\sigma}=\tfrac{1}{5}\pi Z_d{}^{\sigma}\,. \tag{5}$$

Assuming a free-electron shape for the "sp conduction band," the Fermi wave number is given by the density

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of conduction electrons in the usual way. The average number of these conduction electrons per ion is determined by taking the valence of Cu, Al, In, and Sn to be 1, 3, 3, and 4, respectively, and applying the Friedel sum rule[21]

$$Z_{sp}+(Z_d^{\uparrow}+Z_d^{\downarrow})=7 \tag{6}$$

to obtain the number of conduction electrons contributed per Mn ion.

As the magnetic moment per Mn ion is large, the spin splitting is also expected to be large, and we follow Caroli and Blandin in assuming one level (↑) to be filled so that $Z_d^{\uparrow}=5$. The observed magnetic moment $M\mu_B$ then establishes the value of $Z_d^{\downarrow}$ via

$$Z_d^{\uparrow}-Z_d^{\downarrow}=M\,, \tag{7}$$

so that the values of the parameters which determine $\rho_0(\mathbf{R}_{n0})$ are fixed.

Direct calculation of the Bloch wave enhancement factor $\Omega_0|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}$ is difficult even in simple metals and the present case of ordered ferromagnetic ternary alloys is beyond our capacities. To avoid this problem, it is customary to exploit the fact that the Knight shift determines the product of the paramagnetic susceptibility χ_p and the Bloch wave enhancement factor in simple metals. Thus, from the observed Knight shift and a measured or calculated value of χ_p, one can obtain estimates of the enhancement factors appropriate to various ions. Using Knight's[19] data in this way, Caroli and Blandin obtained $|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}$ for Cu and Al. Carrying out the lattice sum in Eq. (2) by summing over the first few nearest-Mn-neighbor shells, they calculated H_{eff} at Cu sites in all three Heusler alloys under present discussion and at the Al sites in Cu_2MnAl.

There are a number of crucial points concerning the estimate of $|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}$ which should be examined. For subsequent discussion, it is convenient to express the enhancement factor in terms of the conventional parameters by

$$|\psi_F(\mathbf{R}_0)|^2{}_{\text{av}}=\xi\frac{3a(s)\text{h.c.}}{16\pi\mu_B g_N\mu_N}. \tag{8}$$

In Eq. (8), g_{N} and μ_{N} are the nuclear g factor and magneton, respectively. The parameter ξ is a measure of the reduction in local s-wave character of the electron wave functions in going from a free atom to the metallic environment, and $a(s)$ is the effective atomic hyperfine constant (in units of cm^{-1}) which we have taken from the recent calculations of Bennett *et al.*[20] Having fixed $a(s)$, the specification of the scale factor ξ determines the Bloch wave enhancement factor as it is the product $\xi a(s)$ which enters Eq. (8).

Of course, the value of ξ appropriate to a given ion depends, in an intricate way, on the electronic structure of the ion's environment. In fact, the present state of knowledge is such that data on solute Knight shifts in dilute alloys is usually used to predict the ξ factors, rather than the reverse, even in simple alloys. It is necessary to adopt the same approach in the present case. To estimate ξ for a given ion X, we shall proceed in two steps. A base line for ξ factors will be established by considering $\xi(X)$ in the Heusler alloys to be approximately the same as $\xi_0(X)$, as determined for a dilute alloy of X in Cu. This implies that the electronic background of Heusler alloys resembles that of pure Cu and requires some comment. The magnetic moment per Mn ion in the Heusler alloys is $\sim 4\mu_B$ just as it is in **Cu**Mn alloys,[22] even for Mn concentrations up to about 20 at.%, and in the manganese brasses.[23] The Fermi energies calculated for the Heusler alloys are only about 10% higher than that of pure Cu. The simple phase diagram of CuMn is also encouraging. On these grounds, we feel that the approximation would not be grossly unreasonable for purposes of establishing general trends, although we anticipate that ξ factors would be overestimated by a factor of 2 or more in the cases of polyvalent ions for which the ξ_0 values are smallest and, thus, most sensitive to changes in the electronic environment. That such a reduction should occur follows from the expectation that the s-wave components of electron wave functions (at the Fermi surface) must be smaller in the more complex Heusler alloys than in Cu which has a lower Fermi energy and a simpler s-type conduction band. The second stage of our specification of ξ factors is given in Sec. IV, where we determine the reduction factors ξ/ξ_0 by comparing calculated (using ξ_0) and measured[10,11] fields at Cu and Al sites in Cu_2MnAl. By extrapolation of these results, hyperfine fields are estimated in Cu_2MnIn and Cu_2MnSn. We proceed similarly in two steps because we expect the ξ_0 factors to provide meaningful reference points and we have more feeling for systematic variations in ξ/ξ_0 than for *ab initio* estimates of ξ itself. In the remainder of this section, we discuss the calculation of hyperfine fields $H_{\text{eff}}{}^{(0)}$ using the binary-alloy approximation for the ξ factors.

The binary-alloy approximation having been stated, the required data for solute Knight shifts in dilute **Cu**X alloys can be taken from the convenient summary given by Bennett *et al.*,[20] and there remains only the question of the paramagnetic susceptibility to be used. Bennett *et al.*[20] have described two methods (B and C of their Table VI) of estimating χ_p which are improvements on the electronic specific-heat method. We took χ_p for Cu to be the average of their two values. This was done partly because a semiphenomenological calculation,[24] which we had done for Cu without knowing of their results, turned out to be very close to the average of their values. The result of using this χ_p is that our hyperfine field strengths are about 25% lower than those obtained using ξ values derived from specific-heat estimates of χ_p. We have summarized in

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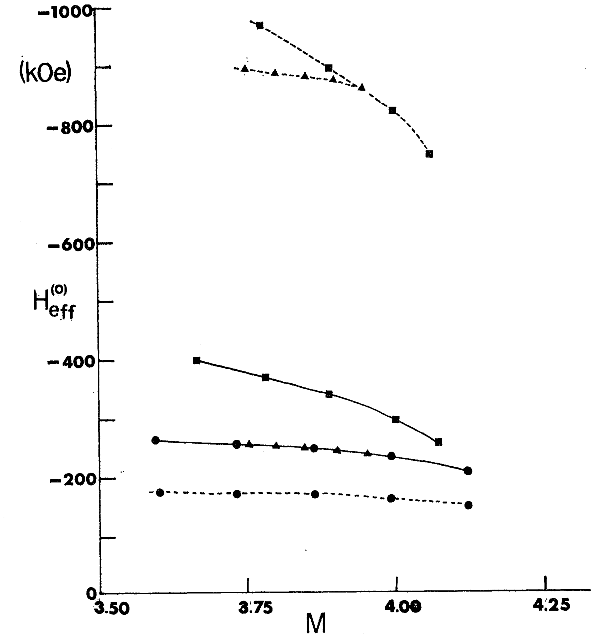

FIG. 1. Hyperfine fields (kOe) in the dilute-alloy approximation as a function of the magnetic moment (μ_B) per Mn ion. Dots, triangles, and squares refer to Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn, respectively. The solid curves refer to Cu fields and the broken curves refer to Al, In, and Sn fields in appropriate alloys.

Table II the values of ξ_0, $a(s)$, and $\xi_0 a(s)/g_N$ which were used. The hyperfine fields were then obtained by carrying out the sums over Mn sites in

$$H_{\mathrm{eff}}^{(0)}(\mathbf{R}_0)=[\Omega_0\xi_0 a(s)/2g_N\mu_N]\sum_n \rho_0(\mathbf{R}_{0n}). \qquad (9)$$

Of course, the hyperfine fields in the ferromagnetic Heusler alloys are temperature-dependent and scale closely with the spontaneous magnetization[10,11]; the fields calculated in Caroli and Blandin's model correspond to the saturation fields obtained by extrapolating the observed fields to $T=0$°K.

The sum in Eq. (9) was evaluated on a computer for Cu and Al in Cu_2MnAl, for Cu and In in Cu_2MnIn, and for Cu and Sn in Cu_2MnSn for a range of values of the magnetic moment per Mn ion. To improve convergence, Eq. (9) was rewritten as a sum over the first N nearest-Mn-neighbor shells plus an integral, weighted by the average density of Mn ions, over more distant shells. This procedure still yielded fluctuations of order 10% at $N=10$ but the convergence was essentially complete after 100 nearest-neighbor shells. The results of the calculations are plotted in Fig. 1 as a function of the Mn ion magnetic moment M. It is seen that the Cu and Al fields are of order -200 kOe and in reasonable correspondence with the results of Caroli and Blandin. These authors did not calculate the In and Sn fields which are of order -900 kOe. To see why these fields are so large, compare Al and In which occupy equivalent sites in their lattices and have the same valence. The total spin polarizations are very similar in both cases. However, $H_{\mathrm{eff}}^{(0)}(\mathrm{In})$ is larger than $H_{\mathrm{eff}}^{(0)}(\mathrm{Al})$ by about the ratio of the corresponding $\xi_0 a(s)/gN$ factors, which is about 5 according to Table II. Similarly, the large Sn fields are primarily due to the relatively large $\xi_0 a(s)/g$ factor. Surveying the available experimental data in Table I, it seems that the binary-alloy approximation yields qualitatively reasonable estimates for the Cu fields. However, it is clear that $H_{\mathrm{eff}}^{(0)}(\mathrm{Al})$ is larger by a factor of about 2.5 than the experimental value[11] and there is little doubt that this failing is a quite general feature of $H_{\mathrm{eff}}^{(0)}$ for the polyvalent ions. Before attempting a phenomenological but systematic discussion, in Sec. IV, of variations in the ratio ξ/ξ_0, we shall calculate the Curie temperature of these Heusler alloys in an attempt to reduce the uncertainty in the value of the magnetic moment per Mn ion which should be used.

TABLE II. ξ_0 factors in binary-alloy approximation, hyperfine coupling constants (cm^{-1}), and resulting $\xi_0 a(s)/g_N$ factors (cm^{-1}) for non-Mn nuclei in the Heusler alloys Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn.

	ξ_0[a]	$a(s)$[a]	$\xi_0 a(s)/g_N$
Cu^{63}	0.40	0.196	0.0529
Al^{27}	0.265	0.141	0.0256
In^{115}	0.26	0.632	0.134
Sn^{119}	0.22	1.36	0.143

[a] Taken from calculations of free-atom wave functions and paramagnetic susceptibility and from dilute-alloy Knight-shift data given in Ref. 20.

III. CURIE TEMPERATURES

The ferromagnetic Curie temperatures, indicated in Table I, of the Heusler alloys are moderately high, which indicates the presence of strong effective magnetic coupling between the Mn ions in spite of their rather large nearest-neighbor distances (>4 Å). Caroli and Blandin showed that these high Curie points could be explained by calculating the paramagnetic Curie temperatures (which are expected to be about 5% higher than the corresponding ferromagnetic Curie temperatures) in a classical mean field approximation. These authors used Caroli's[18] double-resonance model for the magnetic energy of interaction between Mn ions. In this model, the magnetic coupling of a pair of Mn spins, $\mathbf{S}_n$ and $\mathbf{S}_{n'}$, located at $\mathbf{R}_n$ and $\mathbf{R}_{n'}$, respectively, is evaluated in a Hartree-Fock approximation. The resulting effective interaction $E_{nn'}$ is of the usual indirect exchange type but takes into account the virtual bound state, or resonance, at each Mn ion and is given by

$$E_{nn'}=\frac{25\epsilon_F}{2\pi^2S^2}\sin^2\delta_d^{\downarrow}\frac{\cos(2k_FR_{nn'}+2\delta_d^{\downarrow})}{(k_FR_{nn'})^3}\mathbf{S}_n\cdot\mathbf{S}_{n'}, \qquad (10)$$

where we have taken $Z_d^{\uparrow}=5$ and used the asymptotic form on the grounds that $k_FR_{nn'}$ is sufficiently large even for the nearest-Mn-Mn-neighbor distances. This interaction energy defines an effective exchange energy of $-2J(\mathbf{R}_{nn'})$. Treating the spins classically, the paramagnetic Curie temperature T_{c0} is given by $2S^2/(3k_B)$ times the sum of $J(\mathbf{R}_{nn'})$ over all Mn pairs. Thus, in this model,[25]

$$T_{c0}=-\frac{25\epsilon_F}{6\pi k_B}\sin^2\delta_d{}^{\downarrow}\sum_{\substack{n'\\(n'\neq n)}}\frac{\cos(2k_FR_{nn'}+2\delta_d{}^{\downarrow})}{(k_FR_{nn'})^3}. \quad (11)$$

The required lattice sums for T_{c0} of Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn have been evaluated, for a range of values of the Mn ion magnetic moments, using the same procedure as described above for H_{eff}. The results of the calculations are given in Fig. 2. It is evident that T_{c0} is very sensitive to the assumed value of the Mn ion magnetic moment. This is a result of the very slow convergence of the sums in Eq. (11) and their strong dependence on the phase of the oscillatory factor. To be specific, consider the case of Cu_2MnAl. The net contribution to T_{c0} from the first six nearest-Mn-neighbor shells (86 Mn neighbors) is *negative* and the sums still exhibit fluctuations of order 10% even after 100 nearest-Mn-neighbor shells. The reason for this slow convergence is seen by examining the variation of the phase of the cosine in Eq. (11). This phase is very close to $\frac{1}{2}9\pi$ at the first nearest-neighbor shell, so the first shell's contribution is small in spite of its having the largest R^{-3} weight factor. Moreover, as a result of the large Mn-Mn separation, the phase varies rapidly from one shell to the next with the next few shells very nearly alternating between successive troughs and crests of the cosine. Consequently, there is a great deal of cancellation and it is not until many shells have been included that the phase varies sufficiently slowly, from one shell to another, to permit the sums to settle down to their net positive value. (This is quite different from the case of H_{eff} where the spacings between the ions in question were such that the contributions from the near-neighbor shells added much more constructively, resulting in more rapid convergence.) The case of Cu_2MnIn, in which In has a valence of 3, is similar to that of Cu_2MnAl. The sums for T_{c0} of Cu_2MnSn, in which Sn has a valence of 4, have a large positive contribution from the first nearest-neighbor shell. The subsequent convergence is, thus, more rapid but the result is still very sensitive to variations of the phase of the cosine.

Another physically relevant inference may be drawn from the slow convergence of the sums for T_{c0}. All of the above discussion applies to perfectly-ordered samples. For those alloys where the long-range contributions of the interaction play an important role, the magnetic ordering characteristics must be rather sensitive to deviations from stoichiometry and other imperfections. We have attempted to estimate this disordering effect in an *ad hoc* fashion by including a damping factor of the form $\exp(-R_{nn'}/\lambda)$ in Eq. (11) and have recalculated the T_{c0} sums for $\lambda/a_1=10$, 15, and 20, where a_1 is the Mn-Mn nearest-neighbor distance. The effect of this damping factor depends on the relative contributions to the sums of the near and far neighbors which depends, in turn, on M. The results will not be discussed in detail but, to see the magnitude of the effect, a typical set of results will be indicated. For $M=3.80$ and $\lambda=20a_1$, the Curie temperatures for Cu_2MnAl and Cu_2MnIn are reduced by about 30%, while that for Cu_2MnSn is slightly increased by about 5%. The different behavior for the latter alloy is due to the large positive contribution from the first nearest-neighbor shell and, as a result, the reduced sensitivity of the sums to the intermediate and very long-range contributions. The net negative effect of other neighbors is reduced in magnitude so that T_c increases a small amount. It might also be noted at this point that the magnetic hyperfine fields are similarly weakly dependent on the very long-range contributions, so they are affected very little by the damping factor.

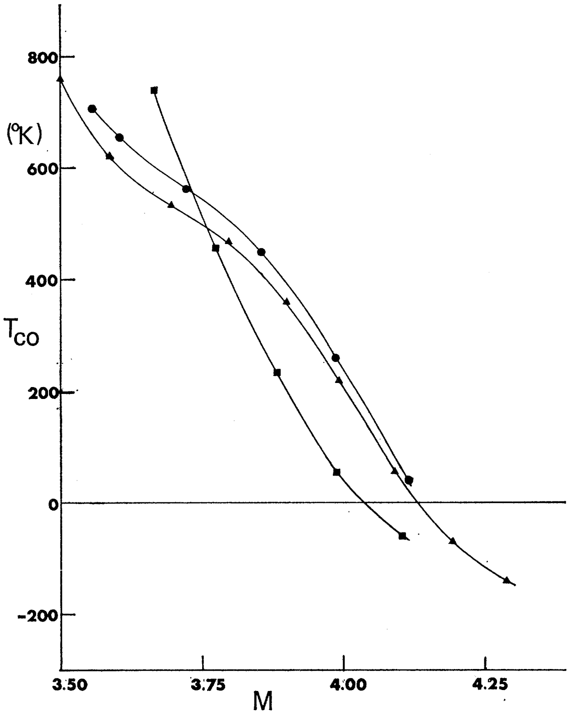

FIG. 2. Paramagnetic Curie temperatures without disorder or $1/S$ corrections (see text). Dots, triangles, and squares refer to Cu_2MnAl, Cu_2MnIn, and Cu_2MnSn, respectively.

There is a further point concerning the Curie temperatures which should be indicated. In Caroli's[18] Hartree-Fock calculation, the interaction energy is determined as a function of the relative orientation of the *average* spin on a given ion. If the resulting coupling $J(\mathbf{R}_{nn'})$ is strictly interpreted in the sense of the isotopic

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[25] Our expressions for $J(\mathbf{R}_{nn'})$ and T_{c0} differ in sign from those of Caroli and Blandin (Ref. 15). We ascribe this difference to typographical errors.

Heisenberg model, the Curie temperature predicted by Eq. (11) should contain an additional factor $S(S+1)/S^2=1+1/S$. Disregarding formal difficulties with the Hartree-Fock treatment, this correction factor (which is unity only for classical spins) increases the estimates of T_c, from Eq. (11), by about 50% since $M\sim4$ implies $S\sim2$. The net effect of this $1/S$ correction and the disorder effect for λa_1 in the range 15–20 is to augment the values of T_{c0} given in Fig. 2 by about 20% for Cu_2MnAl and Cu_2MnIn, and by about 60% for Cu_2MnSn.

It is now appropriate to compare the present calculations with the observed ferromagnetic Curie points θ_f. Oxley *et al.*[5] report $\theta_f=630°K$ for Cu_2MnAl and $\theta_f=500°K$ for Cu_2MnIn. The value for Cu_2MnAl differs somewhat from the early work of Heusler,[1] but that for Cu_2MnIn is in good agreement with the results of Coles, Hume-Rothery, and Myers.[2] The case of Cu_2MnSn is less clear. Carapella and Hultgren[3] found no evidence of the Curie point and observed superlattice lines in their x-ray work even at 900°K. However, Valentiner[4] reported $\theta_f\approx610°K$. It was subsequently noted by Oxley *et al.*[5] that irreversible precipitation of another phase prevented their locating the Curie point of Cu_2MnSn and suggested this phase change as the explanation of Valentiner's result.

In view of the uncertainties in the above calculation of T_c, it is advisable to use the results to determine the range of values of M which yields agreement with experiment while still allowing for considerable variations in the disorder and $1/S$ corrections. To estimate the limits of this range of M for Cu_2MnAl and Cu_2MnIn, it was assumed that an improved treatment of the problem would yield Curie temperatures intermediate between T_{c0} predicted by Eq. (11) and $(1+1/S)T_{c0}$. Using these quite generous limits and the curves in Fig. 2, the corresponding ranges of magnetic moment per Mn ion which give agreement with experiment are found to be 3.74 ± 0.14 for Cu_2MnAl and 3.81 ± 0.11 for Cu_2MnIn. The case of Cu_2MnSn is somewhat different, since θ_f is not known and the effect of the disorder factor is to enhance slightly, rather than reduce T_{c0}. To obtain a rough estimate, we took $\theta_f\sim800°K$ in which case $M\sim3.75$ for Cu_2MnSn; increasing the assumed value of θ_f yields lower estimates for M.

It is clear that the present model is capable of explaining the magnitude of the observed Curie points if M, the parameter specifying the magnetic moment per Mn ion, is appropriately chosen. Caroli and Blandin found good agreement with the experimental Curie points by using values of magnetic moments given by Oxley *et al.*[5] In spite of our $1/S$ correction, which always increases the value of M required to yield a given T_c, we find that the ranges of magnetic moments needed to give agreement with experiment are consistently lower than the values of Oxley *et al.*[5] Consider first the case of Cu_2MnAl for which Oxley *et al.*[5] reported $M=4.12$. Within the context of the present model, this value of M yields a Curie point which is a factor of 10 lower than the observed value. On the other hand, the range of $M=3.74\pm0.14$ suggested by the above analysis is consistent with the results of Endô *et al.*,[6] Felcher *et al.*,[8] and Takata.[9] In the case of Cu_2MnIn, we found that values of M in the range 3.81 ± 0.11 could account for the observed Curie point. In view of the uncertainties involved, we may consider that this estimate overlaps the result $M=3.95$ of Oxley *et al.*[5] as $\Delta M=\pm0.1$ is about the limit of accuracy in these experiments. In fact, the latter authors feel their result to be in close agreement with the value $M=4.04$ reported by Coles *et al.*[2] In the remaining case of Cu_2MnSn we again find that the result $M=4.11$ reported by Oxley *et al.*,[5] in conjunction with present model, cannot explain the order of magnitude of the Curie point. However, this result of Oxley *et al.*[5] is in close agreement with the early value $M=4.14$ of Carapella and Hultgren.[3] Consequently, it appears that the value $M\sim3.75$ resulting from the present calculation is about 10% smaller than these experimental values for Cu_2MnSn.

This is an appropriate point to discuss the approximation of complete spin splitting which has been made in all of the above calculations by assuming that $Z_d^{\uparrow}=5$. We have also carried out calculations to study the effect of incomplete spin splitting. That is, $Z_d^{\uparrow}<5$ but $Z_d^{\downarrow}=Z_d^{\uparrow}-M$ is adjusted to fit the prescribed value of M. In the range of magnetic moments treated, it was found that incomplete spin splitting had a general tendency to reduce T_{c0}. What we considered to be the best results for T_c were always found for $Z_d^{\uparrow}=5$. (The hyperfine fields were also recalculated but were found to be less sensitive to the degree of spin splitting.) Thus, we conclude that the present model, with complete spin splitting, can account for the observed Curie points of Cu_2MnAl and Cu_2MnIn, with values of the magnetic moments in the observed range. The case of Cu_2MnSn is more delicate for a number of reasons and there appears to be a 10% discrepancy between the value of M required in the present analysis and the experimental value.[3,5]

IV. FINAL ESTIMATES OF HYPERFINE FIELDS

In this section, we shall complete our specification of the ξ factors for ions in the Heusler alloys and give more reasonable estimates of the corresponding hyperfine fields. We have already indicated that the ξ_0 factors, deduced from the binary-alloy approximation, are expected to be too large. The hyperfine fields corresponding to the ξ_0 factors will be denoted by H_0 in the following. We assume that the calculation of the net spin polarization at a given non-Mn site by the isotropic asymptotic form Eq. (4), for $\rho_0(\mathbf{r})$ is adequate. The calculated values of H_0 will be compared with the measured fields in Cu_2MnAl, in which all resonances have been observed, and the differences will be attributed to changes in the ionic ξ factors, due to reduced s-wave character, in the Heusler alloy. This will establish the features of the ξ-versus-ξ_0 curve in the typical Heusler alloy Cu_2MnAl. We expect that the $\xi(\xi_0)$ curves for the other Heusler alloys of present interest are very similar and, on the basis of this assumption, the hyperfine fields in Cu_2MnIn and Cu_2MnSn will be estimated.

We have seen in Sec. III that the calculated Curie temperatures are very sensitive to M but that the observed Curie points can be understood. On the other hand, the hyperfine fields shown in Fig. 1 are rather less sensitive to M. We shall, thus, use the value of M deduced from T_c to specify the fields H_0. In the case of Cu_2MnAl, this yields $H_0(\mathrm{Al})=-170\pm5$ kOe and $H_0(\mathrm{Cu})=-255\pm10$ kOe. These values are in reasonable agreement with those of Caroli and Blandin. The observed values are $H(\mathrm{Al})=\pm68.2$ kOe (the sign was not determined) and $H(\mathrm{Cu})=-212$ kOe.[10,11] In keeping with our intention to interpret discrepancies in terms of reduced ξ factors, these results imply $\xi/\xi_0=0.83$ for Cu and $\xi/\xi_0=0.40$ for Al. We see that $\xi(\mathrm{Cu})$ is only slightly reduced but that $\xi(\mathrm{Al})$ is reduced by a factor of 2.5, relative to a pure Cu base, as anticipated for the polyvalent ions with small ξ_0 factors. It may be noted that this value of $H(\mathrm{Al})$ differs considerably from that of ±158 kOe deduced by Fenander *et al.*[12] from their analysis of the nuclear-hyperfine contribution to the specific heat of their (nonstoichiometric) sample of $Cu_{1.937}Mn_{0.960}Al_{1.103}$ and from Caroli and Blandin's estimate of -168 kOe. However, the data of Ogawa and Smit[11] is consistent with that of Sugibuchi and Endô.[10] In particular, it is significant that Sugibuchi and Endô[10] did *not* observe the Al resonance in their range of frequency (100–300 MHz) and temperature (77 to about 400°K). Assuming that their experiment maintained sensitivity at the lower frequencies, one can already conclude from this negative result that the $T=0$°K field strength is less than about 93 kOe. In view of this consistency, we shall assume that the NMR data establishes the form of the $\xi(\xi_0)$ relation for these Heusler alloys.

Consider now the case of Cu_2MnIn in which the field strength at Cu sites is 197.3 kOe (the In resonance was not located).[10] The Cu data provide a limited check on our assumption concerning $\xi(\xi_0)$. From Fig. 1, we find $H_0(\mathrm{Cu})=-250\pm10$ kOe and $H_0(\mathrm{In})=-890\pm15$ kOe. For Cu, comparison of H and H_0 yields $\xi/\xi_0=0.79$, which is only 5% lower than the value for Cu in Cu_2MnAl and, thus, is encouraging. Since Al and In have the same valence, it is reasonable to anticipate the ξ factors scale in the same way in the corresponding Heusler alloys. On this basis, $\xi/\xi_0=0.40\pm0.05$ is estimated for In, which implies that $H(\mathrm{In})=-355\pm45$ kOe. The field at In sites has not yet been observed, although Sugibuchi and Endô[10] located the Mn and Cu resonances in Cu_2MnIn. Taking into account their frequency range and the fact that the highest temperature point on their Cu_2MnIn curve is at about 320°K, one surmises that the In field strength, extrapolated to $T=0$°K, is greater than about 390 kOe. This is based on the assumption that the T dependence of $H(\mathrm{In})$ scales approximately as the magnetization and that there was no appreciable loss of sensitivity at high frequencies. Thus, in Sugibuchi and Endô's[10] experiment, the In resonance was on the verge of observability if our estimates are accurate.

It is more difficult to treat Cu_2MnSn since the higher valence ($Z=4$) of the Sn ion could lead to an additional reduction in its ξ factor. We, thus, expect $\xi(\mathrm{Cu})$ to be slightly reduced in going from Cu_2MnAl to Cu_2MnIn to Cu_2MnSn and estimate $\xi/\xi_0=0.75\pm0.05$ for Cu in Cu_2MnSn. From Fig. 1, $H_0(\mathrm{Cu})=-375\pm15$ kOe, which implies $H(\mathrm{Cu})=-280\pm45$ kOe. Proceeding similarly for the Sn ion for which $H_0(\mathrm{Sn})=-1000\pm50$ kOe and extrapolating to the smaller ξ_0 value, we find $\xi/\xi_0=0.26\pm0.10$ for Sn and $H(\mathrm{Sn})=-260\pm100$ kOe. The Cu field has not yet been measured in this system but the estimated Sn field overlaps the value 200 ± 35 kOe[14] for the Sn field strength at liquid-nitrogen temperature.

As was pointed out by Fenander *et al.*,[12] the specific heat of these Heusler alloys exhibits a nuclear-hyperfine contribution of the form A/T^2, where the coefficient A is given by

$$A=\sum_{\text{sites}}(g_N\mu_N H_{\text{eff}})^2 I(I+1)/3k_B I\,,$$

where I is the nuclear spin at a given site. Thus, A can be easily determined from the hyperfine fields. For the Cu_2MnAl samples on which the NMR data were taken, we find $A=1.515$ mJ °K/mole which is about 20% lower than the result $A=1.89\pm0.04$ mJ °K/mole reported by Fenander *et al.*[12] for their sample. Using our estimate of the In field and the experimental value of the Mn field strength, we obtain (the uncertainty is due to the In field) $A=5.94\pm1.11$ mJ °K/mole for Cu_2MnIn. The specific heat of this alloy has not yet been measured. The case of Cu_2MnSn is again more difficult, as the Mn field has not been estimated. To make a crude estimate, we assume that Cu_2MnSn resembles Cu_2MnIn in that the Mn fields are about 20% stronger than the Cu fields. Then, using our estimates of the Cu and Sn fields, we find $A=3.1\pm1.0$ mJ °K/mole, which is in good agreement with the result of Fenander *et al.*[12] for Cu_2MnSn. We have summarized our estimates of ξ factors, hyperfine fields, and nuclear specific-heat coefficients in Table III.

V. CONCLUSIONS

It is clear that the virtual bound state, or resonance, model of Caroli and Blandin[15] accounts rather well for the qualitative features of these Heusler alloys. In the case of Curie temperatures, good agreement with

TABLE III. Calculated values of ξ/ξ_0 ratios and saturation hyperfine fields (kOe) at Cu sites and X=Al, In, and Sn sites and nuclear-hyperfine specific-heat constants (mJ°K/mole).

	Cu		X		
	ξ/ξ_0	H	ξ/ξ_0	H	A
Cu_2MnAl	0.83	-212^a	0.40	-68.2^a	1.515
Cu_2MnIn	0.79	-197^a	0.40 ± 0.05	-355 ± 45	5.94 ± 1.11
Cu_2MnSn	0.75 ± 0.05	-280 ± 45	0.26 ± 0.10	-260 ± 100	$3.1\ \pm1.0$

[a] These field strengths were taken from experimental data to normalize ξ/ξ_0. See discussion in text.

the observed Curie points is obtained over a well-defined range of values of the parameter M, which yields the saturation magnetic moment per Mn ion. Due to differences in the details of the calculations, the range of M which we find differs from that of Caroli and Blandin[15] who used data of Oxley *et al.*[5] In the case of Cu_2MnAl, which has been most studied, our calculations favor the results of Endô *et al.*,[6] Felcher *et al.*,[8] and Takata,[9] rather than those of Oxley *et al.*[5] Unfortunately, there still is some uncertainty concerning the experimental value of the magnetic moment in these systems.

The hyperfine fields are considerably less sensitive to the assumed value of M. Initial estimates of hyperfine fields were obtained by taking ξ factors or ions in the Heusler alloys to be approximately the same as those (ξ_0) for the corresponding ions in dilute Cu-base binary alloys. However, as anticipated, in order to obtain reasonably accurate estimates of the hyperfine fields (particularly at the sites of polyvalent ions), it is *essential* to take into account the reduction in s-wave character of the Bloch wave enhancement factor in the Heusler alloys. Use of experimental data establishes this reduction factor to be $\xi/\xi_0=0.83$ for Cu and $\xi/\xi_0=0.40$ for Al in Cu_2MnAl. On assuming that these reduction factors are also characteristic of the similar Heusler alloys, Cu_2MnIn and Cu_2MnSn, hyperfine fields in the latter systems have been estimated. The fields at In sites in Cu_2MnIn and at Cu and Sn sites in Cu_2MnSn constitute predictions of the present analysis. The nuclear-hyperfine contributions to the specific heat have also been estimated. These results are summarized in Table III. It should be emphasized that, although these hyperfine fields are the net result of possibly sophisticated polarization processes, in no case has it been necessary to assume the existence of magnetic moments in the Cu ion cores to explain the large hyperfine fields.

There is not yet a complete set of consistent data for these Heusler alloys. It would be very useful to complete the determination of the magnitudes and of the signs (thus far only known for Mn and Cu) in Cu_2MnAl of the hyperfine fields in well-ordered samples and to understand the sensitivity of the data to deviations from stoichiometry and to heat treatment. Further specific-heat work would also provide important information, particularly in the case of Cu_2MnIn, which is predicted to have a fairly large nuclear-hyperfine contribution.