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CHARGE AND RELATED SPIN PERTURBATIONS IN MAGNETIC METALS : AN INTERPRETATION OF MÖSSBAUER SPECTRA OF THE HEUSLER ALLOYS Pd$_{2}$MnSn$_{1-x}$Sb$_{x}$

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1. Introduction. — Mössbauer measurements of the magnetic hyperfine fields at both $^{119}$Sn and $^{121}$Sb nuclei in the ferromagnetic Heusler alloy solid solution series Pd$_{2}$MnSn$_{1-x}$Sb$_{x}$ $(0 < x < 1)$ were reported at the last ICAME /1/. They showed a very large increase ( >30T) in the fields at both types of nuclei as x increased from 0 to 1. Using a simple model, the possibility is examined that these increases arise from the long-range oscillatory effects of the electrostatic screening of Sn and Sb ions. Changes in both the charge and spin densities of a comparable magnitude to those observed can be obtained, so it is concluded that this mechanism may be important and warrants a more realistic calculation.

2. Charge and spin perturbations in magnetic metals. — The screening of a localized charge perturbation in an electron gas gives rise to the so-called Friedel oscillations /3/ of charge density in the gas that extend many Angstrom units away from the perturbation. They arise as a result of interference effects at the Fermi surface and have an oscillation period that depends on $k_p$, the Fermi wavevector. If the electron gas is magnetically polarized, then $k_p \neq k_p$ and there will be accompanying oscillations of spin-density in the gas. The generalized susceptibilities that describe these effects were introduced by Kim et al. /4/. More recently Kolk /5/ has emphasized the importance of accounting for the spin-dependence of the wavelength of electrons at the Fermi level in a magnetically concentrated metal to calculations of the oscillatory charge- and spin-densities.

In this paper the possibility will be examined that the hyperfine field and spectrum shift variations arise primarily from changes in the electrostatic screening at a site where an Sb ion is substituted for Sn. To the best of our knowledge this is the first time that such a mechanism has been considered in this context.

Résumé. — Bien que la composition semble avoir peu d'influence sur le paramètre du réseau et le moment magnétique dans les alliages ferromagnétiques de Heusler du type Pd$_{2}$MnSn$_{1-x}$Sb$_{x}$ $(0 < x < 1)$, la spectrométrie Mössbauer met en évidence une assez large augmentation des densités de charge et de spin à la fois sur $^{119}$Sn et $^{121}$Sb quand x croît de 0 à 1. A partir d'un modèle simple, on tente d'expliquer cet accroissement par l'existence d'oscillations à grandes distances des charges d'écran des ions Sn et Sb.

Abstract. — Despite only very small changes with composition of the lattice parameter and magnetic moment in the ferromagnetic Heusler alloy series Pd$_{2}$MnSn$_{1-x}$Sb$_{x}$ $(0 < x < 1)$, Mössbauer measurements show quite large increases in the charge and spin densities at both $^{119}$Sn and $^{121}$Sb nuclei as x goes from 0 to 1. Using a simple model, the possibility is examined that these increases arise from the long-range oscillatory effects of the electrostatic screening of Sn and Sb ions. Changes in both the charge and spin densities of a comparable magnitude to those observed can be obtained, so it is concluded that this mechanism may be important and warrants a more realistic calculation.

In this paper the possibility will be examined that the hyperfine field and spectrum shift variations arise primarily from changes in the electrostatic screening at a site where an Sb ion is substituted for Sn. To the best of our knowledge this is the first time that such a mechanism has been considered in this context.

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Table I

<table>
<thead>
<tr>
<th>Probe nucleus</th>
<th>Pd$_2$MnSn</th>
<th>Pd$_2$MnSb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{1}(4.2K)$ (T)</td>
<td>$\delta^{2}(4.2K)$ (T)</td>
</tr>
<tr>
<td>$^{119}$Sn</td>
<td>-3.1</td>
<td>1.492</td>
</tr>
<tr>
<td>$^{121}$Sn</td>
<td>-20.5</td>
<td>0.76</td>
</tr>
</tbody>
</table>

(1) Magnetic hyperfine fields measured at 4.2 K. The fields measured at $^{121}$Sn are larger than those reported elsewhere because a larger value for the ratio of the nuclear moments was used (Rush et al., to be published).

(2) Spectrum shifts measured at room temperature. $^{119}$Sn shifts are measured with respect to the Ca $^{118}$SnO$_3$ source (at room temperature) while $^{121}$Sn shifts are relative to InSn at 4.2 K.

(3) Change in the electronic charge density at the nuclear site on going from Pd$_2$MnSn to Pd$_2$MnSb, calculated as outlined by Shirley /13/. Values assumed for the nuclear $\delta r/r$ for $^{119}$Sn and $^{121}$Sn taken from Ruby et al. /13/, were:

$$\delta r = (1.2 \times 10^{-4})$$

and

$$\delta r = (-8.5 \times 10^{-4})$$

More recent determinations of these quantities show large variations and above values at least appear to lie within the range of later values. Uncertainties in both are probably about ±50%.

(4) Change in the electronic spin density at the nuclear site on going from Pd$_2$MnSn to Pd$_2$MnSb, assuming that the fields arise entirely from the Fermi contact interaction.

These long-range perturbations will depend on the local scattering at the Z site and therefore will differ in Pd$_2$MnSn from Pd$_2$MnSb. The aim here is to examine these changes using a very simple model to see if they can account for the observed differences in hyperfine field and spectrum shift.

3. Model calculation. The following simple model was set up for the purpose of making an order-of-magnitude estimate of the changes of electronic spin- and chargedensities introduced by changing the scattering potentials at the Z sites.

The conduction electrons were approximated by plane waves that, for the purpose of calculating their probability density at nuclear sites, were orthogonalized to the core states of the Z ions. The conduction electron gas was assumed to be uniformly polarized at low temperature such that $k_F^2-k_F^2 = 2k_F^2$, where $k_F$ is the average wavevector of the Fermi level.

Effects of coherent scattering were neglected, so that the net spin- and charge-densities at a point due to scattering by the surrounding ions was just the sum of the contributions from each indivi-

dual ion. As a result of this, and because only the changes in the spin- and charge-densities on going from Pd$_2$MnSn to Pd$_2$MnSb were of interest, the scattering from other than the Z site ions was ignored. Many of the effects of hybridization and scattering at the Pd and Mn sites will be incorporated in the phenomenological polarization parameter $\epsilon$.

The effect of scattering by a "probe" ion on the spin and charge densities at its nucleus was also ignored. A more complicated two-centre scattering calculation is required to properly include the effects of local scattering at the probe ion site.

The scattering centres (Z site ions) were represented by spherically symmetric square potential wells whose dimensions were constrained to satisfy the Friedel sum rule. The probe nucleus was taken to be at the origin and the extra charge density $\delta n(r)$ produced there by a potential well at a distance $r$ was calculated using the formulae of Alfred and Van Oostenburg /6/ including terms up to $r^{-6}$ and assuming the electron gas to be completely degenerate.

The uniform polarization of the gas was then introduced and the additional charge- and spin-density produced at the origin by the potential well at $r$ was calculated numerically from:

$$\delta n(r) = \delta n^s(r) + \delta n^f(r)$$

where $\delta n^f(r)$ is the extra charge density produced by scattering of the spin $\sigma$ conduction electrons.

Figure 1 shows examples of the results of this calculation for parameters whose significance will be explained in the next section. The difference between the "asymptotic" calculation of the charge density, which contains only lowest order terms in $1/r$ (i.e. $r^{-3}$), and the higher-order approximation used here is illustrated in figure 1(a). The damped oscillatory behaviour of $\delta n(r)$ and $\delta p(r)$ is seen to be modulated for $c \neq 0$ as pointed out by Kolb /5/.

The total "excess" charge- and spin-densities at the origin were then found by summing the effects of all of the surrounding Z-site ions out to 12th nearest neighbours, or all 248 Z ions within a radius of ~15.7 Å. This procedure was done only for the end members of the solid solution series, i.e. x = 0 and 1, although the nucleus at the origin could be either $^{119}$Sn or $^{121}$Sn. The scattering centres around the origin were then all the same and were characterized by $Z = 4$ ("Pd$_2$MnSn") or $Z = 5$ ("Pd$_2$MnSb") where $Z$ is the number of valence electrons of the scattering atom.
In the vicinity of the probe nucleus, the conduction states may be approximated by plane waves orthogonally to the probe ion core. This leads to an enhancement of the conduction electron density at the nucleus by a factor of about 400 for both Sn and Sb, this factor being calculated using Hartree-Fock-Slater self-consistent wave-functions for the ion cores. Taking this enhancement into account gives:

\[ \Delta n(0) \approx 0.27 \text{ a.u.} \quad (T > T_c) \]
\[ \Delta \rho(0) \approx 0.37 \text{ a.u.} \quad (T < T_c, \varepsilon = 0.05) \]

where \( \Delta \) represents the change on going from the simulated \( \text{Pd}_2\text{MnSn} \) lattice to that for \( \text{Pd}_2\text{MnSb} \). These values are of the same order of magnitude as those deduced from the measurements and shown in the last two columns of Table I.

The values of \( k_F \) used to describe the conduction electrons (Table II) were chosen to give \( \Delta n(0) \) and \( \Delta \rho(0) \) values of the same sign, and are larger than is often assumed from standard prescriptions of the number of conduction electrons contributed by each atom (see /1/ for Refs.) but are smaller than the value (1.0 a.u.) used in a recent calculation of Mn-Mn exchange interaction in \( \text{Pd}_2\text{MnSn} \) /1/.

However, the relationship of this parameter to the real band structure is not clear. The two values (0.87 a.u. for "\( \text{Pd}_2\text{MnSn} \)" and 0.92 a.u. for "\( \text{Pd}_2\text{MnSb} \)"") are internally consistent in the sense that \( k_F^2 \) increases by about 18% on going from \( \text{Pd}_2\text{MnSn} \) to \( \text{Pd}_2\text{MnSb} \), which is roughly the expected increase in the number of conduction electrons.

The value taken for the band-splitting parameter \( \varepsilon \) is that obtained from the formula of Kolk /5/:

\[ \varepsilon = \frac{J_0}{2E_F} \frac{\sum_{\alpha} g_{\alpha}^2}{N} \]

where the symbols have their usual meanings /5/.

Using the estimates \( |J_0| \approx 2eV \) as is obtained for CuMn alloys /13/ and \( E_F \approx 10eV \) and \( \sum_{\alpha} g_{\alpha}^2 / N \approx 1 \) gives \( \varepsilon \approx 0.05 \), and this was the value taken (Table II).

### 5. Conclusions

It appears from this approximate calculation that the long-range effects of the...
screening of impurity atoms in metals may be important in the interpretation of hyperfine interaction measurements, as was concluded by Kolk /11/ although for a different situation. He was concerned with the effects of local lattice distortion around an impurity whereas in the case considered here the scattering centres are changed while the distance between them remains approximately constant.

It is recognized that the calculation presented here is very much a first approximation but it indicates the potential importance of these effects and the need for a more realistic examination of them.

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References

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/12/ Shirley, D.A., Rev. Mod. Phys. 36 (1964) 319.