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Local magnetic ordering of Fe impurities in Pd_2MnSn

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Abstract. Mössbauer effect of Fe^{57} embedded as very dilute substitutional impurities in Pd_2MnSn was studied. The impurities are seen to replace the three elements in the alloy. Although the Curie temperature of the alloy is 189K, well below the room temperature, the Mössbauer spectrum recorded at room temperature consisted of two distinct 6-finger magnetic hyperfine spectra and a single unsplit line. One of the 6-finger patterns which corresponds to an internal magnetic field of $H_{int}=-375$ kOe is inferred to arise due to local magnetic coupling of the localized magnetic moments of Fe impurities at the Pd sites with those of the 4 Mn first nearest neighbours of the Fe impurities. The other 6-finger pattern which corresponds to an internal magnetic field of $H_{int}=-335$ kOe is inferred to arise due to the local magnetic coupling of the localized magnetic moments of the Fe impurities at the Sn sites with those of the 6 Mn second nearest neighboours of the Fe impurities. The difference in the internal magnetic fields observed at the Pd and Sn sites in the alloy could be understood qualitatively, on the basis of RKKY theory, as arising due to the different conduction electron polarization contributions to the net internal magnetic field at the Fe impurity sites. The results of the measurements suggest that the localized magnetic moments of Fe^{57} impurities at Pd and Sn sites are antiferromagnetically coupled with the moments of their neighbouring Mn atoms.

Keywords. Mössbauer effect; magnetic ordering; magnetic alloys; magnetic interactions.

1. Introduction

During the last few years considerable experimental (Maletta and Rao 1972) and theoretical (Kim 1970) work has been directed towards understanding the influence of local atomic environment on the formation of localized magnetic moments on transition metal impurities. It is now experimentally well established that the formation of a localized moment on a transition metal impurity in another transition metal matrix depends critically on the nature, the number and the interatomic distance of nearest neighbours of the impurity (Maletta and Rao 1972, Huffman 1971, Sellmyer and Kaplow 1971). Further, Sellmyer and Kaplow (1972) have explained ferromagnetism in certain dilute alloys as a result of cooperative effect among neighbouring localized magnetic moments as against a band phenomenon. Inoue and Moriya (1967) have shown theoretically that the interaction between a pair of localized moments mediated by conduction electrons via the well known s-d exchange inter-

action would lead to ferro- or antiferromagnetic coupling between the two moments depending on the separation between them and on the details of the Fermi surface.

In the present paper it is shown experimentally that very dilute Fe^{57} impurities embedded at Pd and Sn sites in the Heusler alloy (Webster 1969), Pd_2MnSn exhibit local magnetic ordering, even at a temperature well above the Curie temperature of the alloy, due to local magnetic coupling of the localized moment of an Fe impurity with those of its neighbouring Mn atoms.

2. Experimental technique and results

The Mössbauer spectra of Fe^{57} embedded as dilute substitutional impurities in the Heusler alloy, Pd_2MnSn was studied using Co^{57} diffused in the alloy as the source (Co^{57} decays to an excited state of Fe^{57} following electron capture). The alloy Pd_2MnSn was prepared by repeated melting of the constituent elements of high purity in proper proportions in an arc furnace. X-ray diffraction measurements of the alloy prepared showed that the crystal structure was of the Heusler alloy type (figure 1), with a lattice parameter of 6·37 Å in agreement with the value reported by Webster (1969). Two thin disks of about 1 cm^2 area were cut from the ingot for preparing Mössbauer sources subjected to different heat treatments. The disks were annealed at 600°C for about 50 hr and then at 900°C for about 3 hr. Small quantities of Co^{57} activity was diffused into each of the disks following standard techniques. One of the sources was annealed at 900°C for 2 hr and slowly cooled to the room temperature. The other source was also annealed at 900°C for 2 hr, but subsequently quenched in water.

The Mössbauer spectrum of the slow-cooled source was recorded at 293 K utilizing a thick absorber of $K_4Fe(CN)_6 3H_2O$ containing 2 mg Fe^{57}/cm^2 (figure 2). The spectrum consists of a very prominent but broad central unsplit line and a 6-finger hyperfine pattern. The hyperfine lines are broad and of small intensity. The Mössbauer spectrum of the source recorded utilizing a thin absorber of $K_4Fe(CN)_6 3H_2O$ containing 0·1 mg Fe^{57}/cm^2 (figure 3 a) reveals that the 6-finger hyperfine pattern seen in figure 2 in fact consists of two distinct 6-finger hyperfine patterns. The outer 6-

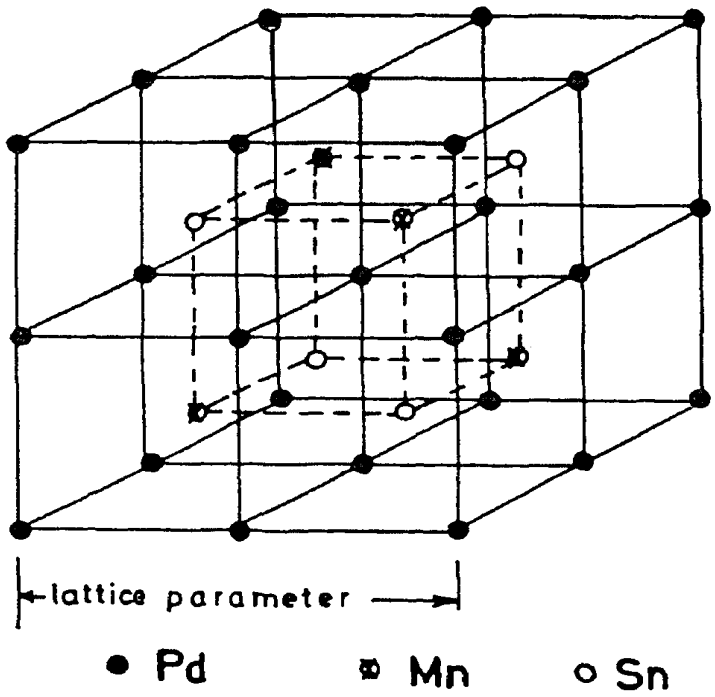

Figure 1. Heusler alloy structure

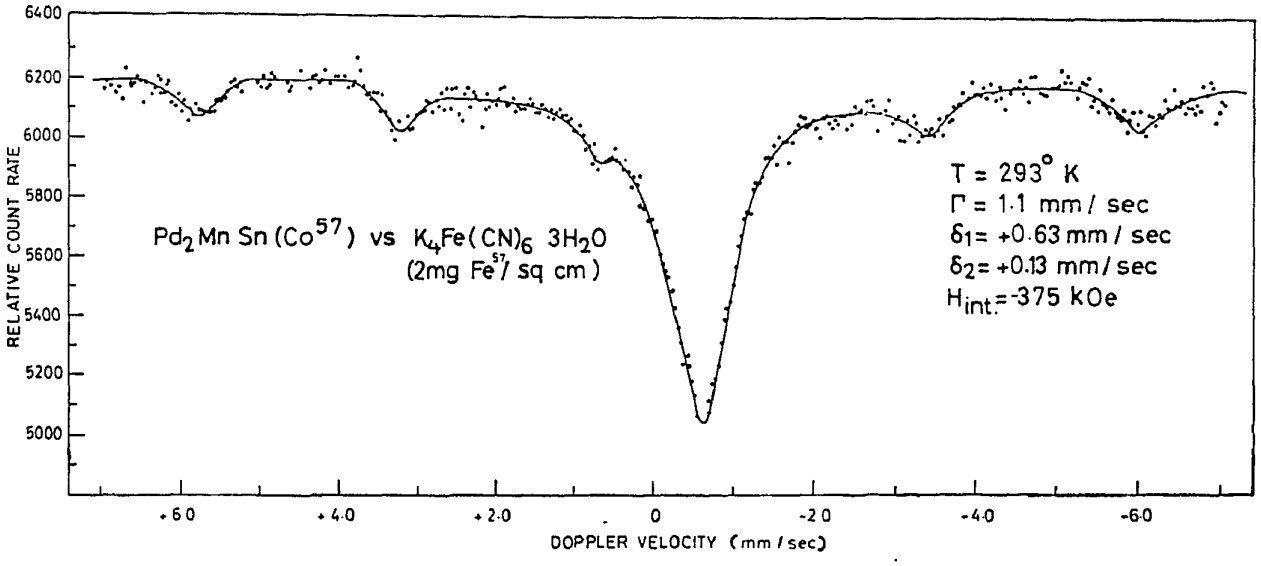

Figure 2. Mössbauer spectrum of $Pd_2MnSn(Co^{57})$ at 293 K. Enriched $K_4Fe(CN)_6 3H_2O$ containing 2 mg Fe^{57}/cm^2 was used as an absorber.

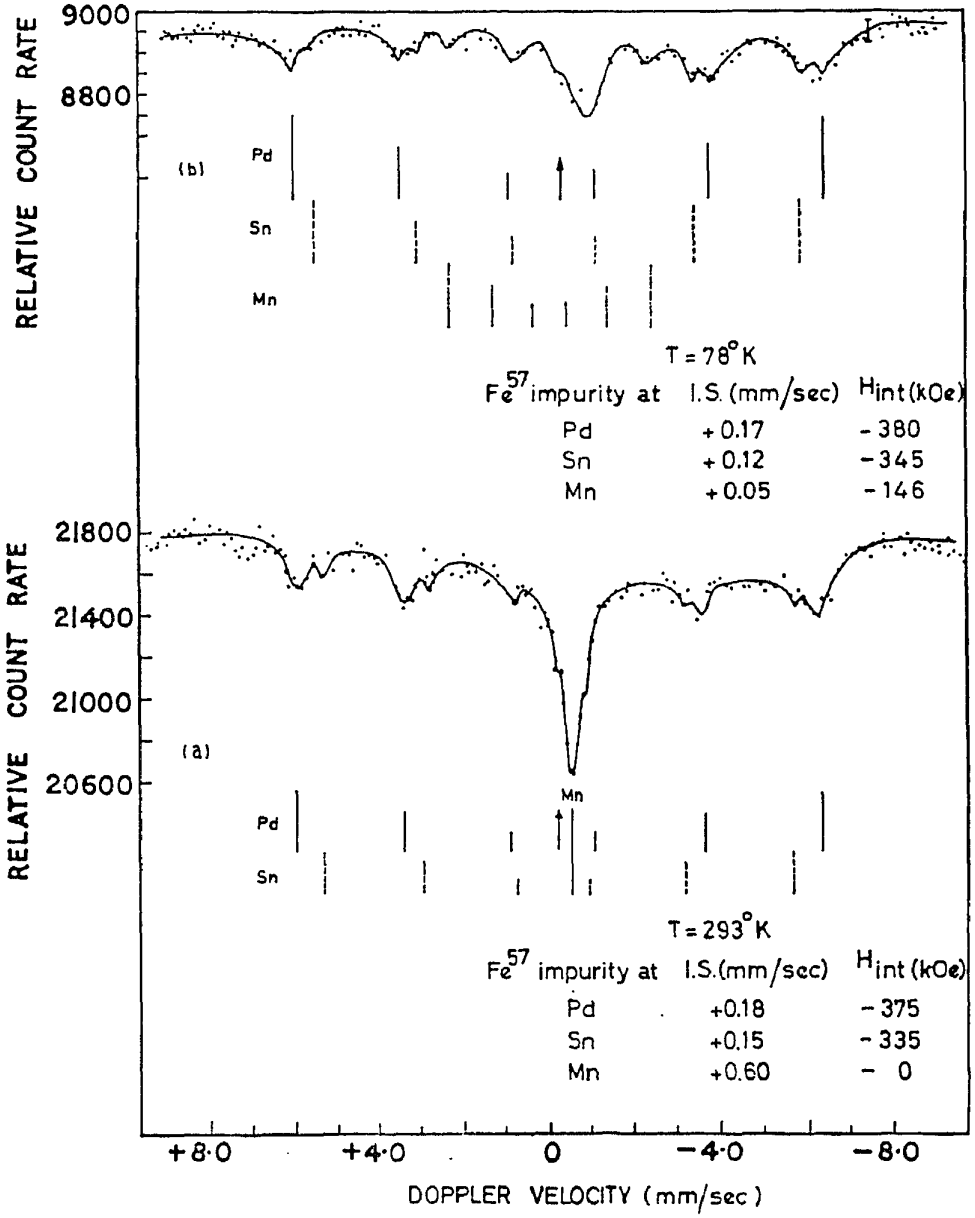

Figure 3. Mössbauer spectra of Fe^{57} impurities in Pd_2MnSn (a) at 293 K and (b) at 78 K. The absorber used was $K_4Fe(CN)_6 3H_2O$ containing 0·1 mg Fe^{57}/cm^2.

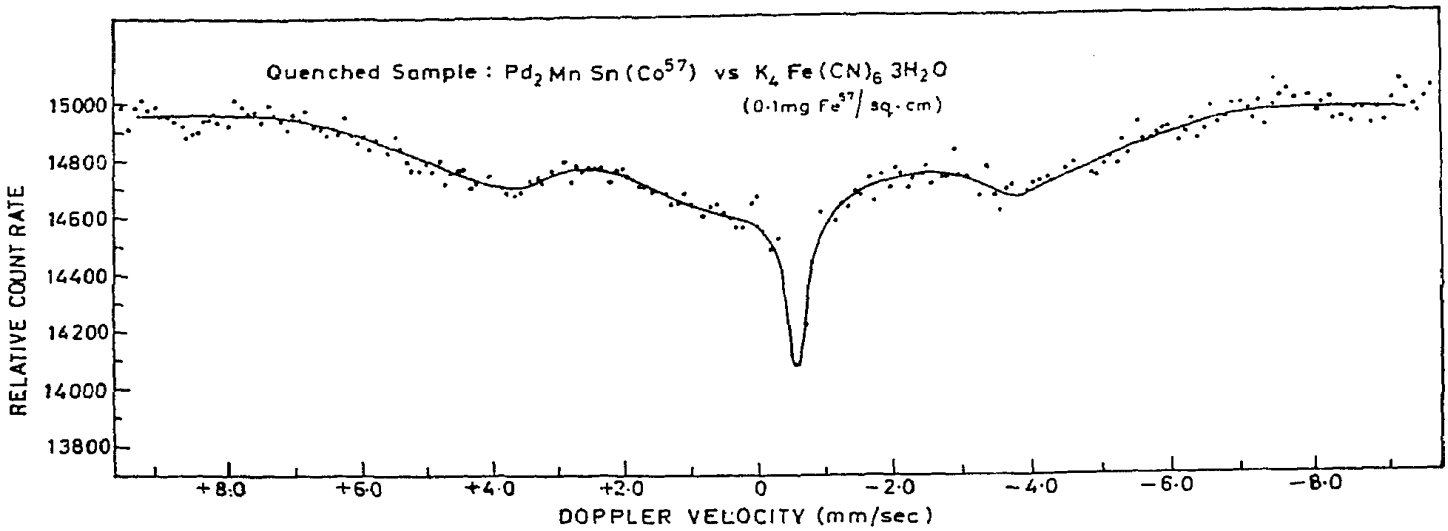

Figure 4. Mössbauer spectrum of $Pd_2Mn\,Sn(CO^{57})$ at 293 K. The source was quenched from 900°C. $K_4Fe(CN_6)3H_2O$ containing 0·1 mg Fe^{57}/cm^2 was used as an absorber.

finger pattern corresponds to an internal magnetic field of $H_{int}(1) = -375$ kOe and the inner to $H_{int}(2) = -335$ kOe (The negative sign of the internal fields is assumed as it is usually the case for the Fe nuclei). The Mössbauer spectrum of the source recorded at 78 K utilizing the thin absorber is shown in figure 3 b. The spectrum consists of three 6-finger hyperfine patterns. The single unsplit line observed at 293 K is seen to diminish in itensity appreciably at 78 K and give rise to an additional 6-finger pattern corresponding to an internal magnetic field of $H_{int}(3) = -146$ kOe. The magnitudes of the two internal fields observed at 293 K are seen to increase by about 5 to 10 kOe at 78 K. The spectra (figure 3 a, b) clearly indicate the presence of three distinct and magnetically inequivalent Fe^{57} sites in the alloy. The small absorption lines at the positions indicated by arrows in figure 3 seem to arise due to the presence of a small impurity phase in the alloy.

The Mössbauer spectrum of the quenched source recorded at 293 K utilizing the thin-absorber is shown in figure 4. It consists of a central line with broad wings on both sides of the central line. The spectrum clearly indicates the presence of a distribution of internal magnetic hyperfine fields at different Fe^{57} impurities in the alloy.

3. Discussion

The Heusler alloy (Webster 1969) Pd_2MnSn has perfectly ordered $L2_1$ structure shown in figure 1. The Pd atoms occupy the A- and C- sites while Mn and Sn atoms occupy the B- and D- sites respectively. In the present case the A- and C- sites are equivalent. The magnetic properties of the alloy have been extensively studied. It is well established that the alloy is ferromagnetic below 189 K and that each Mn atom carries a localized magnetic moment (Natera *et al* 1970) while Pd and Sn atoms do not carry any magnetic moment.

3.1. *Slow-cooled* Pd_2MnSn (Co^{57})

In the case of the slow-cooled Mössbauer source, the diffused Fe^{57} impurities are seen to replace the three elements and occupy the three inequivalent sites in the alloy as revealed by the observation that each of the Mössbauer spectra recorded is a resultant of superposition of three contributions from three distinct and magnetically inequivalent sites in the alloy. *A priori*, from a consideration of the relative sizes of the

atoms replaced, it is logical to presume that Fe^{57} impurities replace the three elements in the alloy preferentially in the order of Mn, Pd and Sn. Consequently, from an inspection of the relative intensities of the three contributions to each of the observed Mössbauer spectra, the single unsplit paramagnetic line observed at 293 K and the additional 6-finger pattern observed at 78 K can be understood as arising from the Fe^{57} impurities located at the Mn-sites in the alloy. The 6-finger hyperfine patterns corresponding to the maximum internal magnetic field in each of the Mössbauer spectra observed (figure 3) can be understood as arising due to the Fe^{57} impurities located at Pd-sites and the remaining 6-finger pattern in each spectrum as arising due to the Fe^{57} impurities located at Sn-sites in the alloy.

The most striking and interesting result of the present experiment is that the Fe^{57} impurities situated at Pd and Sn sites exhibit local magnetic ordering at a temperature, well above the Curie temperature of the alloy, while the bulk of the sample is in a paramagnetic state. It appears that the localized moments of Fe^{57} impurities situated at Pd sites are magnetically coupled with those of the 4 Mn first nearest neighbours located at a distance of 2·74 Å from the Fe impurities. The localized moments of the Fe^{57} impurities situated at Sn-sites seem to be magnetically coupled with those of the 6 Mn second nearest neighbours located at a distance of 3·19 Å from the Fe impurities. On the other hand, the Fe^{57} impurities situated at Mn sites in the alloy do not seem to get magnetically coupled with their 12 Mn third nearest neighbours, which are relatively at a larger distance of 4·52 Å from the Fe impurities, as indicated by the paramagnetic line observed at 293 K. It is not difficult to understand such a phenomenon in the light of the detailed theoretical work of Inoue and Moriya (1967). It is shown that the interaction energy between two neighbouring localized moments mediated by the conduction electrons via the s-d exchange interaction would lead to ferro- or antiferromagnetic coupling between the two localized moments depending on the separation between them and on the details of the Fermi surface. The absence of any local magnetic ordering at room temperature of the Fe impurities situated at Mn sites may probably be due to comparatively larger separation (4·52 Å) between the Fe impurities and the 12 Mn third nearest neighbours of the impurities which results in weakening the strength of the interaction between the two moments. The relatively weak interaction can reduce the magnitude of the magnetic moment on the impurity as compared with the magnitudes of localized moments present on the Fe impurities situated at Pd and Sn sites; consequently, below the Curie temperature of the alloy a smaller internal magnetic field is expected at Fe impurities situated at Mn sites compared to those present at Pd and Sn sites as has, in fact, been observed experimentally.

The conduction electron polarization (CEP) by localized moments via the s-d exchange interaction in a Heusler alloy is a well known effect. By observing the behaviour of internal field at the Fe impurities at different sites in the alloy one can, under certain favourable circumstances, directly study the radial dependence of the conduction electron polarization.

The internal magnetic field experienced by an Fe impurity nucleus in a cubic material such as Pd_2MnSn with no spin-orbit coupling arises due to the well known Fermi contact interaction which consists of two parts :

1. The polarization of the core s-electrons due to the exchange interaction with the 3d electrons. This gives rise to a large negative field contribution.
2. The polarization of the 4s conduction electrons which in turn consists of three parts :

(a) The polarization of the paired 4s conduction electrons due to the exchange interaction with the 3d electrons of the impurity. This gives rise to a positive field contribution.

(b) The polarization of the paired 4s conduction electrons arising from the admixture of the 4s conduction electrons with the 3-d band.

(c) The polarization of the 4s conduction electrons at the Fe impurity site arising due to any localized moments on neighbouring atoms via the s-d exchange inter-

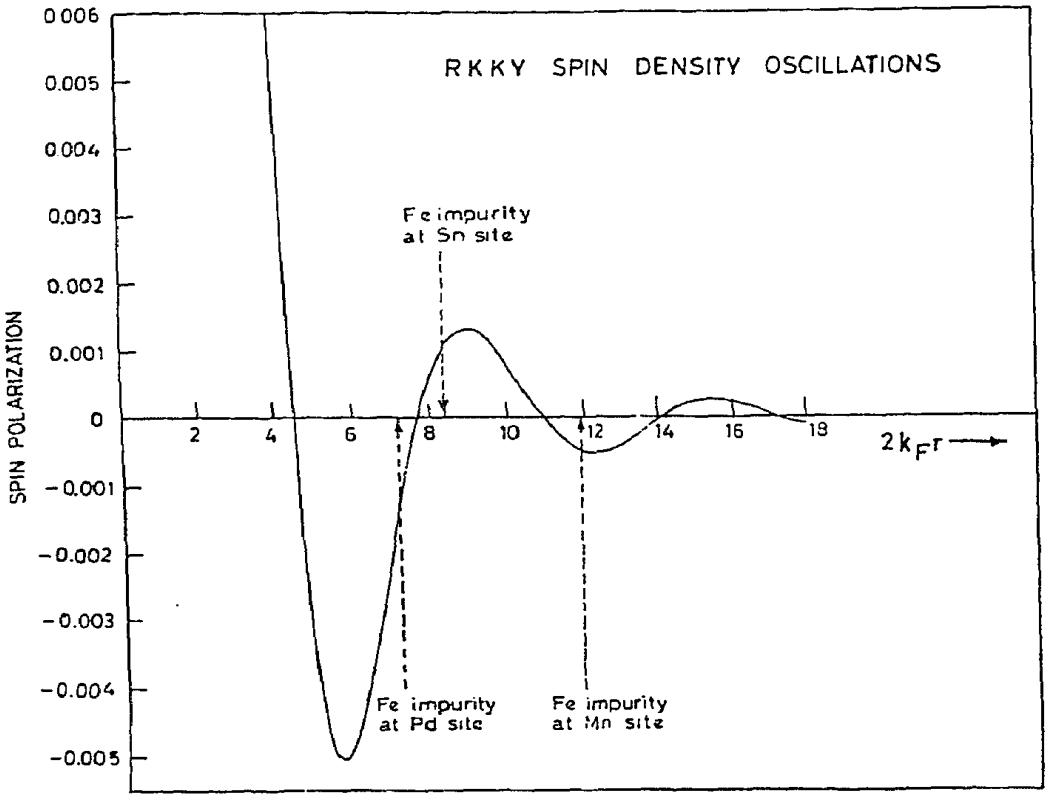

Figure 5. Unnormalized conduction electron spin polarization in Pd_2MnSn due to the localised magnetic moment on a Mn atom at the origin versus $2k_F r$. Positions of Fe^{57} impurities occupying Pd- Sn and Mn sites are also shown.

action. The sign of the polarization is determined by the Fermi wave vector, k_F and the position of the impurity with respect to the positions of neighbouring atoms carrying localized moments.

If the contributions (1), 2(a) and 2(b) remain constant at the Fe impurities at different sites in the alloy, which is the case if the magnitudes of localized moments on the Fe impurities at different sites are equal, then any changes in the internal fields at different Fe impurity sites will be due to the mechanism 2(c). In the present experiment, it seems reasonable from the observed large internal fields at Pd and Sn sites to presume that the localized moments on the Fe impurities at the two sites have attained their maximum values and are of equal magnitude while the magnitude of the moment at Mn sites is comparatively much less. The difference in the internal fields observed at the Pd and Sn sites can thus be understood as arising due to different total CEP contributions from the localized moments of neighbouring Mn atoms.

The radial dependence of CEP due to a localized moment on a Mn atom on the basis of the approximate RKKY theory (Watson 1967) with the crude assumption of a constant exchange integral $\mathcal{J}_{s-d}(0)$, described by the function $F_{RKKY}(x) = x^{-4}(x \cos x - \sin x)$ with $x = 2k_F r$, is shown in figure 5. For the calculations of the function

$F_{RKKY}(x)$ shown in figure 5, the Fermi wave vector k_F has been estimated assuming contributions of 4 electrons from each Sn atom, 1·2 electrons from each Mn atom and none from the Pd atoms to the conduction band in the alloy. The spin density at a distance r from a Mn atom is given by the expression (Yosida 1957)

$$\Delta\rho(r) = -\frac{8(3n)^2}{E_F V}\frac{\mathcal{J}_{s-d}(0)}{\mathcal{N}}\ 2k_F r\, F(2k_F r)$$

It is seen that the CEP contributions to the internal fields at the Pd and Sn sites are of opposite signs.

Now, if it is assumed that the exchange integral $\mathcal{J}_{s-d}(0)$ is negative, which is quite logical for the Fe impurities in transition metal matrices, then the experimentally observed fact that the magnitude of the internal field at the Pd site is larger than that at the Sn site suggests that the localized moments on Fe impurities at both the Pd and Sn sites are antiferromagnetically coupled with those of their neighbouring Mn atoms or alternatively that the moments of Fe impurities at Pd sites are ferromagnetically coupled with those of their Mn first nearest neighbours while the moments of Fe impurities at Sn sites are antiferromagnetically coupled with those of their Mn second nearest neighbours. The neutron diffraction measurements (Natera *et al* 1970) of Pd_2MnGe have revealed that the alloy is slightly disordered and that about 2% of the Mn atoms occupy the Pd sites in the alloy with their moments antiferromagnetically coupled with those of their neighbouring Mn atoms. As the lattice parameters of Pd_2MnSn ($a_0 = 6{\cdot}37$ Å) and of Pd_2MnGe ($a_0 = 6{\cdot}18$ Å) are not very much different, it is possible that the Fe impurities at Pd sites in the former alloy also have their moments antiparallel to those of the Mn atoms. If the moments of Fe impurities at Pd sites in Pd_2MnSn are antiparallel to those of the first nearest Mn atoms of the impurities, then the results of the present experiment indicate that the moments of Fe impurities at Sn sites are also antiparallel to those of the second nearest Mn atoms of the impurities at Sn sites.

3.2. *Quenched* Pd_2MnSn (Co^{57})

The Mössbauer spectrum of the quenched source (figure 4) is seen to be drastically different from that of the slow-cooled source (figure 3). The former indicates that the Fe^{57} impurities in the quenched source experience a distribution of the internal magnetic field as against well defined fields experienced by the Fe^{57} impurities in the slow-cooled source. It is likely that quenching of the source leads to disorder of the alloy and/or clustering of the Fe impurities in the alloy.

Another interesting and significant result of the present study is that the isomer shift observed at the Fe impurities occupying the Mn sites decreases considerably from a value of 0·6 mm/sec in the paramagnetic state to 0·05 mm/sec in the ferromagnetic state of the alloy while the shifts observed at the other two sites do not vary appreciably. This change in the isomer shift observed indicates that the density of the 3d- states of the Fe impurities at the Mn sites is more in the paramagnetic state as compared to that in the ferromagnetic state of the alloy. This increase or ' motional narrowing ' of the 3d- density of states in the transition from the ferromagnetic to the paramagnetic state observed confirms the recent theoretical predictions of Daniel (1971).

The technique of time-differential perturbed angular correlations (TDPAC) is one of the possible precision experimental methods which can yield information that is strikingly similar to that obtained from the Mössbauer effect experiments, particularly

with regard to magnetic hyperfine interactions in solids. TDPAC is well suited in determining magnetic hyperfine fields in particular at dilute magnetic impurities in a system. Although Fe^{57} is not a sensitive probe for TDPAC experiments due to small anisotropy of the 122-14 keV cascade, Hohenemser *et al* (1969) have shown from their TDPAC experiments on Fe^{57} impurities in a Ni host that the technique can be utilized for determining the magnetic hyperfine field, both in sign and magnitude, present at the Fe^{57} impurity sites in the Ni host.

We intend to carry out TDPAC experiments on the present system to verify the results obtained from the Mössbauer effect experiments.

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