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Evidence for magnetically induced electronic and phonon anomalies in cubic Pd_2MnSn

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Abstract. ^{119}Sn Mössbauer spectra of the Heusler alloy Pd_2MnSn have been studied in the temperature range $4.2\ K \leqslant T \leqslant 298\ K$. Although the temperature dependence of the Sn magnetic field is found to scale with the host magnetisation, the recoil-free fraction and the isomer shift display an anomalous temperature variation. As the temperature is reduced from above the Curie temperature T_C, the recoil-free fraction is found to increase while the contact electron density $|n(0)|^2$ is found to decrease anomalously. The former result provides evidence for magnon–phonon coupling while the latter provides evidence for electron–magnon coupling which is mediated by phonons.

1. Introduction

Normally the temperature dependence of the magnetic hyperfine field $H(T)$ at solute impurities and host atoms in ferromagnetic crystals closely follows that of host magnetisation $M(T)$. There are several instances, however, where an anomalous behaviour has been documented (Cranshaw 1969, Raghavan *et al* 1977, Collins *et al* 1977). These anomalies apparently occur at solute impurities in Co when H changes sign in the middle of the 4p and 5p shells (figure 1). The physical origin of this intriguing behaviour has not been fully understood as yet. In the $Pd_2MnSb_{1-x}Sn_x$ system (Tenhover and Boolchand 1978), a crossover from negative to positive fields has been observed to occur as a function of composition x. For convenience, this is shown in figure 2, which is taken from the work of Tenhover and Boolchand (1978). The Sn field changes from $-34.5(5)$ kOe at $x = 1.00$ to 240(4) kOe at $x = 0.01$. Indeed, if anomalies in H appear near the zero-field crossover, then it would seem that this Heusler alloy (HA) provides an ideal host to investigate such effects. Clearly, one can approach the zero crossover from negative as well as positive fields by merely choosing the appropriate composition x. Guided by these considerations, we therefore chose to investigate the well characterised end member ($x = 1.00$), namely Pd_2MnSn, since the $M(T)$ of this material was measured earlier by Webster and Tebble (1967).

Our ^{119}Sn Mössbauer experiments show that although $H(T)$ closely follows $M(T)$, exhibiting no temperature anomaly, the isomer shift $\delta(T)$ and recoil-free fraction $f(T)$ both change anomalously in the ferromagnetically ordered phase. The consequences of these

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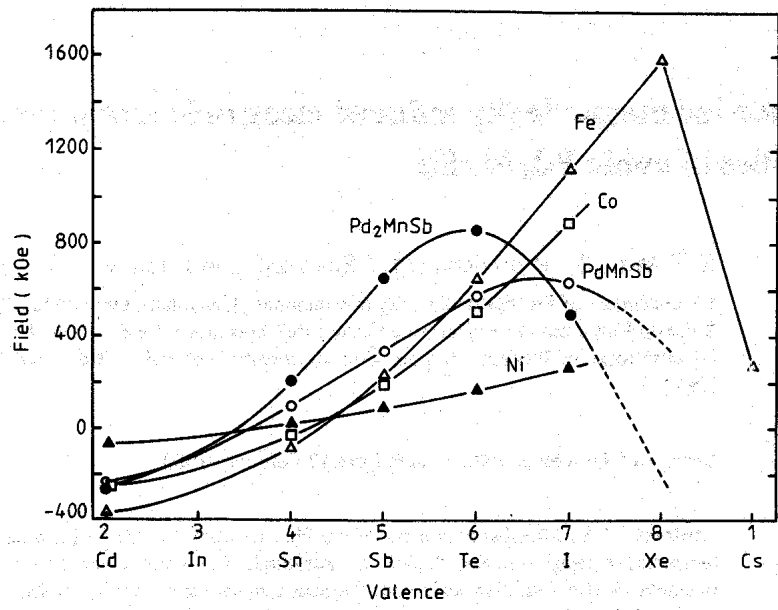

Figure 1. Trends of measured magnetic hyperfine fields at 5 sp impurity atoms in Pd_2MnSb, PdMnSb, Fe, Co and Ni hosts.

observations on the origin of $H(T)$ and the lattice dynamics of Pd_2MnSn are discussed later in this paper.

2. Experimental considerations

Using 99.99% pure Pd and Mn from Spex Industries and 99.9999% pure Sn from the Mineral and Chemical Corporation as starting materials, we prepared the sample by

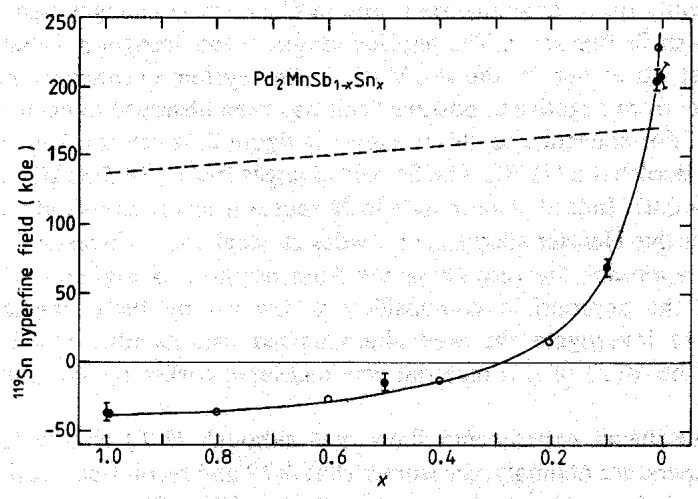

Figure 2. ^{119}Sn fields in $Pd_2MnSb_{1-x}Sn_x$ observed as a function of Sn composition x. The full circles represent the results from Tenhover and Boolchand (1978), while the open circles are from Price *et al* (1976). The broken line gives the predictions of these fields based on the Jena–Geldart model.

induction-melting stoichiometric amounts of the desired elements in a graphite boat in a quiescent argon gas. The typical wt% loss during preparation was under 1%. To prepare absorbers for the Mössbauer measurements, we powdered the ingot obtained in this way. This powdered sample will henceforth be denoted as the virgin sample. There is good evidence that the powdering process leads to substantial plastic deformation of the Pd_2MnSn lattice. In order to remove this damage, we sealed the virgin sample in an evacuated (less than 10^{-6} Torr) quartz tube and annealed it at 600 °C for different time periods. The sample was then slowly cooled to room temperature in six hours.

We also made the samples by sintering the elements at 1100 °C in an evacuated quartz ampoule. The materials were retained at that temperature for two days followed by a quench to room temperature. After being powdered, the samples were annealed at 600 °C for several time periods.

The Mössbauer effect experiments were performed using a conventional spectrometer (Tenhover and Boolchand 1978) and a liquid-helium exchange-gas dewar with the absorber mounted in the insulation space. The temperature of the absorber could be changed continuously over the range 35–300 K using a heater assembly. The long-term (24 hours) temperature stability of the system was ± 2 K. ^{119m}Sn in vanadium was used as the source and held at 78 K.

3. Experimental results

3.1. X-ray diffraction

X-ray diffraction patterns were obtained on a Super precession camera using a variable temperature refrigerator (Air Products 101A Cryo Tip) in the temperature range $83 \leqslant T \leqslant 298$ K. At room temperature both the virgin and annealed samples revealed three principal reflections: (220), (400) and (422). These are characteristic of the Heusler $L2_1$ structure. The unit cell length of the induction-melted sample was found to be 6.380(2) Å in agreement with previous measurement (Webster and Ramadan 1977). Furthermore, no evidence was found of either intensity changes in the permitted reflections relative to one another or of the appearance of new superlattice reflections over the temperature range examined. This indicates that our Pd_2MnSn retains the cubic $L2_1$ structure below T_C and also that the thermal expansion of this material does not exhibit any unusual behaviour in the examined temperature range.

3.2. Heat treatment

It has been shown (Blizzard *et al* 1979, Tenhover *et al* 1980, Shinohara *et al* 1981) that the HA undergo substantial plastic deformation on cold working such as powdering at room temperature. These effects can lead to a line broadening of Bragg peaks in x-ray diffraction as well as a line broadening of the nuclear gamma resonance lineshape.

We found that annealing the virgin samples resulted in greater crystallographic ordering as evidenced by a narrowing of the x-ray (220), (400) and (422) reflections as well as a narrowing of the gamma resonance linewidth (figure 3). For the latter measurements a linewidth of 0.88(2) mm s^{-1} was observed at 295 K using a carefully annealed Pd_2MnSn (0.50 mg cm^{-2}) sample. Moreover, striking enhancement in the absorption area under the resonance line was found as a function of annealing (figure 3). Specifically, samples cooled

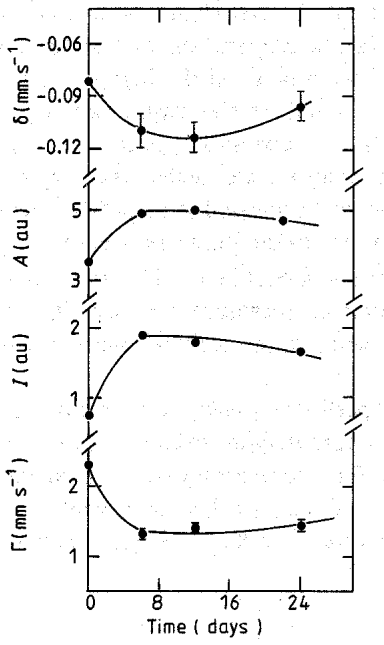

Figure 3. Annealing effects shown in the Mössbauer spectra of Pd_2MnSn at 78 K; δ denotes the isomer shift of Sn in Pd_2MnSn relative to ^{119m}Sn in vanadium, A is the resonant absorption area, I is the unit peak intensity and Γ is the observed linewidth.

slowly from 600 °C yield 40% more resonance absorption than quenched samples. These quenching effects must clearly be related to the presence of defect-induced phonon anomalies in this HA (Shinohara *et al* 1981).

Since the sintered samples appeared to be less homogeneous than the induction-melted ones, we chose to investigate the spectra as a function of temperature for the latter samples only.

3.3. Mössbauer effect

Figure 4 shows typical spectra of Pd_2MnSn taken as a function of temperature. The Curie temperature T_C of our sample was established to be 184(1) K from a temperature scan of the resonant signal intensity (per cent effect) at the centre of gravity of the spectra (figure 5). The spectra were analysed in the usual way as a superposition of six lines keeping g_e/g_0 fixed at 0.2134 (Greenwood and Gibb 1971). Figure 6 summarises the observed temperature variations of the magnetic field $H(T)$, the isomer shift $\delta(T)$, the linewidth $\Gamma(T)$ and the absorption area $A(T)$.

There are two striking results that emerge from these measurements. One is the anomalous variation in $A(T)$ or $f(T)$, which exhibits a step-like increase in the range $T_C - 5 < T < T_C$. The second is the variation in $\delta(T)$ which shows a dramatic decrease in $|n(0)|^2$ at the onset of magnetic ordering. On the other hand, $H(T)$ displays a normal behaviour in the sense that it scales well with $M(T)$ (Webster and Tebble 1967). The saturation value $H(T \rightarrow 0)$ is found to be $-34.5(5)$ kOe and this is in good agreement with previous measurements (Kanekar *et al* 1968, Le Dang Khoi *et al* 1970, Geldart *et al* 1972). The negative sign of this field was established earlier by Geldart *et al* (1972) on application of an external magnetic field.

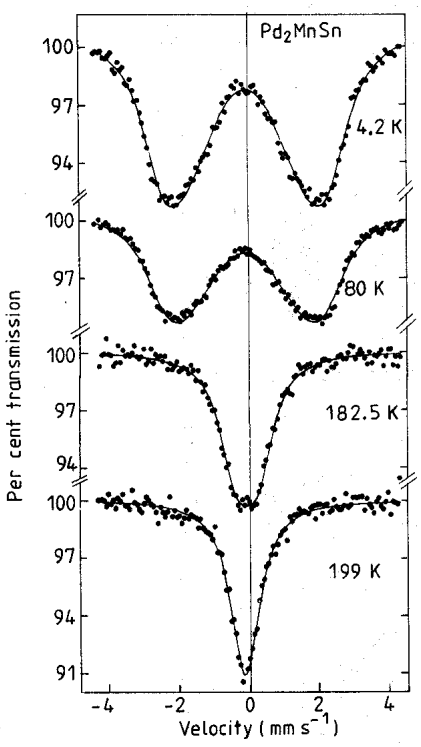

Figure 4. The Mössbauer spectra of Pd_2MnSn at the temperatures indicated.

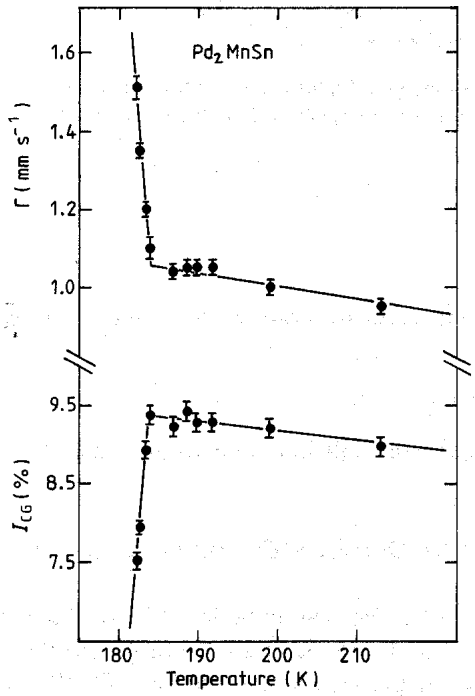

Figure 5. The temperature dependence of the linewidth and centroid velocity transmission near the Curie temperature in Pd_2MnSn.

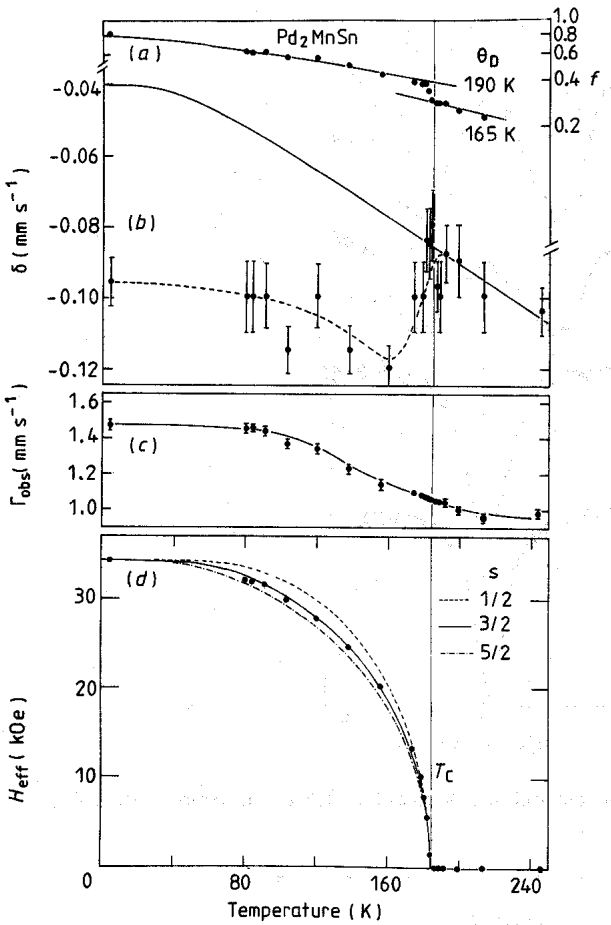

Figure 6. The temperature variation of (*a*) the recoil-free fraction, (*b*) the isomer shift, (*c*) the observed linewidth and (*d*) the internal magnetic field at the Sn site in Pd_2MnSn.

4. Discussion

4.1. Isomer shift

It is well known that the isomer shift measures the contact electron density $|n(0)|^2$ through the usual relation

$$\delta = \tfrac{2}{3}\pi Z e^2 \Delta\langle r^2\rangle \Delta |n(0)|^2. \tag{1}$$

The temperature dependence of this shift can be looked upon as arising from two terms:

$$\delta(T) = \delta_{\mathrm{SOD}}(T) + \delta_{\mathrm{chem}} \tag{2}$$

where $\delta_{\mathrm{SOD}}(T)$ is the usual second-order Doppler shift term while δ_{chem} is related to the chemistry of the probe atom.

From the high-temperature ($T > T_C$) linear variation in $f(T)$ we have obtained the Debye temperature θ_D of Pd_2MnSn to be 165(5) K and have projected the second-order Doppler shift (SOD) contribution δ_{SOD} to the isomer shift at low ($T < T_C$) temperatures. This contribution (δ_{SOD}) appears in figure 6 as a continuous curve. It permits us to establish the chemically induced part of the shift, i.e. $\delta(T) - \delta_{\mathrm{SOD}}(T)$, which is plotted in

figure 7. Interestingly, $\delta(T)-\delta_{SOD}(T)$ shows a striking similarity to $H(T)$. This similarity suggests that the origin of this chemically induced shift is magnetic in character. Such shifts have been examined extensively in the past, particularly for the case of Fe in the magnetic critical region (Preston 1968, Kobeissi *et al* 1978). Our case provides the first clear evidence of a magnetically induced isomer shift. The negative sign of $\delta(T)-\delta_{SOD}(T)$ implies that $|n(0)|^2$ reduces at the Sn nuclei when the HA orders ferromagnetically.

To understand the origin of the abrupt change of isomer shift at T_C, we have considered two specific mechanisms, i.e. a direct electron–magnon coupling and an indirect electron–magnon coupling mediated by phonons. For the first case, we studied the response of conduction electrons in the paramagnetic and ferromagnetic region using density functional theory (Hohenberg and Kohn 1964, Kohn and Sham 1965, von Barth and Hedin 1972, Rajagopal and Calloway 1973). The net spin moment of the conduction electrons in the paramagnetic region is zero whereas in the ferromagnetic phase the conduction band is split into majority and minority spin sub-bands. Since the effective potential seen by electrons depends on this spin polarisation (Jena *et al* 1978a, b), one may expect to see a change in the conduction electron charge density (and hence the isomer shift) at the probe nucleus.

The density functional equation for the electrons in the ground state can be written as

$$(-\tfrac{1}{2}\nabla^2 + V^{\sigma}_{\text{eff}}(\boldsymbol{r}))\psi^{\sigma}_{k}(\boldsymbol{r}) = \varepsilon^{\sigma}_{k}\psi^{\sigma}(\boldsymbol{r}) \tag{3}$$

where $\psi^{\sigma}_{k}(\boldsymbol{r})$ is the single-particle wavefunction for an electron with spin σ, wavevector k and energy ε^{σ}_{k}. $V^{\sigma}_{\text{eff}}(\boldsymbol{r})$ is the effective spin-dependent potential. Here, we have used Hartree atomic units ($\hbar=1$, $e=1$ and $m=1$). The density of electrons with spin σ is given by summing over the occupied states, namely

$$n^{\sigma}(\boldsymbol{r}) = \sum_{k}^{\text{occ}} |\psi^{\sigma}_{k}(\boldsymbol{r})|^2. \tag{4}$$

The electron charge density is given by

$$n(\boldsymbol{r}) = n_{\uparrow}(\boldsymbol{r}) + n_{\downarrow}(\boldsymbol{r}). \tag{5}$$

The effective potential $V^{\sigma}_{\text{eff}}(\boldsymbol{r})$ is given by

$$V^{\sigma}_{\text{eff}}(\boldsymbol{r}) = V_{\text{es}}(\boldsymbol{r}) + V^{\sigma}_{\text{xc}}(n^{\sigma}(\boldsymbol{r})) \tag{6}$$

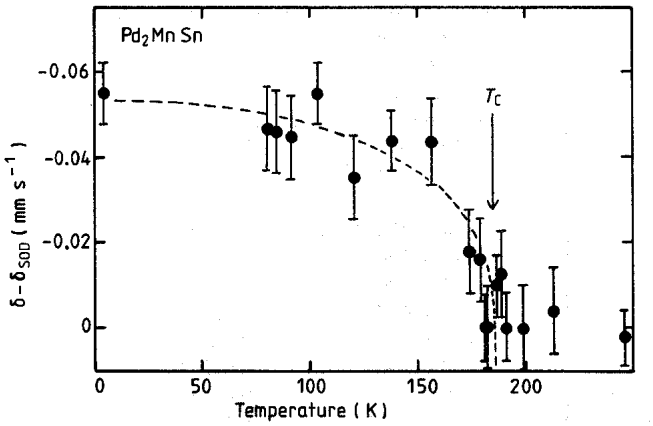

Figure 7. The temperature variation of the chemically induced ^{119}Sn isomer shift for $T<T_C$ in Pd_2MnSn.

where V_{es} is the electrostatic potential due to all the charges in the medium and V_{xc}^{σ} is the exchange-correlation potential for an electron with spin σ in the local density approximation (Gunnarsson *et al* 1974). V_{es} is related to the charge density through the Poisson equation

$$\nabla^2 V_{es} = -4\pi(n_+(\boldsymbol{r}) - n(\boldsymbol{r})) \tag{7}$$

where $n_+(\boldsymbol{r})$ is the distribution of positive charges in the medium. In the continuum model

$$n_+(\boldsymbol{r}) = A\delta(\boldsymbol{r}) + n_0\theta(\boldsymbol{r} - \boldsymbol{R}_{WS}) \tag{8}$$

where A is the atomic number of the probe nucleus ($A = 50$ for Sn), θ is the Heaviside function, R_{WS} is the radius of the Wigner–Seitz sphere surrounding the Sn site and n_0 is the homogeneous density of the positive charges of the medium. Equations (3)–(8) were solved self-consistently for Pd_2MnSn both in the paramagnetic and ferromagnetic phases. The calculated eigenvalues for all the occupied core electrons and the total electron density at the Sn nucleus are given in table 1. The energy associated with the spin splitting of an orbital as compared to the orbital energy is smaller for the inner cores than that for the outer cores. This is, as expected, due to the predominance of the Coulomb interaction between the nucleus and the inner core orbitals. Since the bulk of the electron density at the nucleus is due to the inner s electrons, the significant difference between the energy levels of spin-up ($\uparrow$) and spin-down ($\downarrow$) electrons of the outer orbitals has no noticeable effect on the nuclear site electron density. This is reflected in the total electron density in the paramagnetic and ferromagnetic phases of Pd_2MnSn as given in the last row of table 1. We should point out that the electron density in table 1 contains contributions from both

Table 1. Energy eigenvalues of the occupied core orbitals and electron density at the nuclear site of Sn in the ferromagnetic and paramagnetic phase of Pd_2MnSn. The energy is in Hartree atomic units (27.2 eV).

Orbital	Spin	Ferromagnetic energy	Paramagnetic energy
1s	$\uparrow$	−1026.23536	−1026.26912
	$\downarrow$	−1026.30260	−1026.26912
2s	$\uparrow$	−151.00142	−151.03513
	$\downarrow$	−151.06857	−151.03513
2p	$\uparrow$	−141.29825	−141.33197
	$\downarrow$	−141.36543	−141.33197
3s	$\uparrow$	−28.60459	−28.63834
	$\downarrow$	−28.67178	−28.63834
3p	$\uparrow$	−24.59650	−24.63025
	$\downarrow$	−24.66369	−24.63025
3d	$\uparrow$	−17.13591	−17.16964
	$\downarrow$	−17.20308	−17.16964
4s	$\uparrow$	−4.02763	−4.06136
	$\downarrow$	−4.09473	−4.06136
4p	$\uparrow$	−2.69369	−2.72743
	$\downarrow$	−2.76080	−2.72743
4d	$\uparrow$	−0.49066	−0.52427
	$\downarrow$	−0.55751	−0.52427
5s	$\uparrow$	−0.00662	−0.01811
	$\downarrow$	−0.03267	−0.01811
$n(0) = (a_0^{-3})$	$\uparrow$	43739.44	43739.33
	$\downarrow$	43739.34	43739.33

core and conduction electrons, although the latter is very small compared with the contribution of the former. The near equality of the densities in table 1 leads us to the conclusion that the observation of a significant change in the isomer shift at the Curie point is not due to purely electronic effects induced by the onset of magnetism.

We next consider the effect of the electron–phonon interaction on the electron density at temperatures in the vicinity of the Curie point. The conduction electron wavefunction can be written in terms of an infinite-order perturbation theory

$$\psi_k(\boldsymbol{r}) = \psi_k^{(0)}(\boldsymbol{r}) + \sum_G \frac{\langle \psi_{k+G}^{(0)}(\boldsymbol{r}) | V(\boldsymbol{r}) | \psi_k^{(0)}(\boldsymbol{r}) \rangle}{E_k - E_{k+G}} + \dots \tag{9}$$

where $\psi_k^{(0)}(\boldsymbol{r})$ is the zeroth order wavefunction for wavevector k, G is the reciprocal lattice vector and E_k is the single particle energy. The crystal potential $V(\boldsymbol{r})$ is given by

$$V(\boldsymbol{r}) = \sum_\nu v(\boldsymbol{r} - \boldsymbol{R}_\nu) \tag{10}$$

where $v(\boldsymbol{r} - \boldsymbol{R}_\nu)$ is the potential due to an ion located at $\boldsymbol{R}_\nu$. Following Kasowski (1969), we can write the temperature dependence of the potential matrix element as

$$\langle \psi_{k+G}^{(0)} | V | \psi_k^{(0)} \rangle = \exp(-W(G, T)) \langle \psi_{k+G}^{(0)} | V^{(0)} | \psi_k^{(0)} \rangle \tag{11}$$

where $V^{(0)}$ corresponds to the potential of a static lattice. All the temperature dependence in equation (11) is now contained in the Debye–Waller factor $W(G, T)$. The electron density can be calculated by summing over the occupied Fermi volume, namely

$$n(\boldsymbol{r}) = \sum_k^{\text{occ}} |\psi_k(\boldsymbol{r})|^2. \tag{12}$$

For the isomer shift calculations, we only need $n(0)$ which is the electron density at the nuclear site $\boldsymbol{r} = 0$.

Substituting equation (11) into equation (9) and keeping only those terms linear in the Debye–Waller factor $W(G, T)$ in the expansion of the exponential, it shows that (Jena 1976)

$$n(0) = n^0(0) - \alpha\varphi(T) \tag{13}$$

where $n^0(0)$ is the electron density at the nuclear site when all the ions are held fixed. α is a constant that depends upon the potential and other parameters of the static lattice and is generally found to be positive (Jena 1976, Jena *et al* 1978a, b). $\varphi(T)$ is the Debye integral and is related to the Debye–Waller factor. Thus the change in the electron density at the magnetic phase transition as one approaches from above the Curie point is

$$\Delta n(0) = n_{T \to T_C + \varepsilon}(0) - n_{T \to T_C - \varepsilon}(0) = \alpha(\varphi(T \to T_C - \varepsilon) - \varphi(T \to T_C + \varepsilon)) \tag{14}$$

in the limit $\varepsilon \to 0$.

For our Pd_2MnSn sample (see figure 6 and § 4.2), we find that as T approaches T_C from above, the Debye–Waller factor abruptly decreases, i.e.

$$\varphi(T \to T_C + \varepsilon) > \varphi(T \to T_C - \varepsilon). \tag{15}$$

Substituting this result into equation (14), we see that $\Delta n(0)$ is negative. In other words, the electron density at the Sn site decreases as one approaches T_C from above and passes through the phase transition. This is in clear agreement with our observed anomaly in $\delta(T)$. A quantitative result of $\Delta n(0)$ in equation (14) is more difficult to obtain from theory since

this computation involves a detailed study of the band structure of Pd_2MnSn. In addition, we would also need a quantitative estimate of the change in the Debye–Waller factor due to magnon–phonon coupling.

Thus we conclude that the observed change in the isomer shift at T_C is brought about by a coupling of phonons to electrons and magnons. The magnon–phonon coupling influences W, which in turn affects the electron density through phonon–electron coupling.

4.2. Recoil-free fraction

The second striking result to emerge from our data is the anomalously large (35%) increase in $f(T)$ near T_C as shown in figure 6. Since the absorber thickness ($t_A = 1$) is small, thickness broadening effects will not be present at T_C. Therefore, no expected anomalous increase in f will be observed from this thickness-related change. However, large increases as well as decreases in f across T_C have been observed previously by Feder and Nowik (1979a) in the cubic Laves phase materials RCo_2 and RFe_2 (R denotes rare earths). These authors showed that in the presence of a magnon–phonon interaction, line broadening as well as a frequency shift of phonon modes can occur (Feder and Nowik 1979b). These two competing factors cause f to either increase or decrease anomalously with temperature near T_C.

It is well known that $-\ln f$ is related to the -1 moment ($\langle\omega^{-1}\rangle$) of the phonon spectrum and therefore weighs heavily for low-frequency acoustic modes in a solid. We believe that in our case there is a magnon-induced shift ($\omega \rightarrow \omega + \Delta\omega$) of phonon modes to higher frequencies, i.e. there is a hardening of the $L2_1$ lattice that causes the f factor to increase anomalously. Indeed, one can expect elastic constants of this material to exhibit anomalous changes as well. We are not aware of such measurements on this material, which would clearly be of interest.

4.3. Magnetic field

The origin of magnetism in the conducting ferromagnetically ordered cubic, Mn-based HA X_2MnY has been the subject of numerous experimental and theoretical papers. Trends of experimentally measured fields at 5 sp impurity atoms (Y site) in Pd_2MnSb and PdMnSb (de Waard *et al* 1978, Boolchand *et al* 1978) are shown as a function of the impurity valence in figure 1. Starting from negative fields at the lower end of the 5 sp shell, the fields cross over to positive values near $Z = 4$ and appear to saturate at the upper end of the shell. Jena and Geldart (1974) and Blandin and Campbell (1973) have shown theoretically and independently that this trend can be qualitatively reproduced if the spin polarisation induced at sp impurity atoms arises from the scattering of spin-polarised conduction electrons.

The normal behaviour of Sn $H(T)$ observed in Pd_2MnSn is in sharp contrast to that reported for the same atom in the Co host (Cranshaw 1969). In the crystal structure of Pd_2MnSn, Sn happens to be a second neighbour of the magnetic Mn atom. It is therefore reasonable to expect that any direct s–d overlap polarisation will be minimal. This is clearly not the case for the Sn impurity atom in Co, where a direct s–d overlap exchange term must also provide an important second mechanism to induce spin polarisation at the diamagnetic Sn atoms in addition to conduction electron polarisation. We, therefore, suspect that anomalies in $H(T)$ reported in the Co host (Cranshaw 1969, Raghavan *et al* 1977) are most likely to derive from an anomalous temperature variation in the direct s–d overlap exchange constant $J_{sd}(T)$. One of the difficulties in calculating this constant is the

lack of a precise knowledge of the local lattice relaxation around the impurity. It would seem that the latter information would be directly accessible by looking at the Sn absorption edge in EXAFS measurements. Indeed, such measurements performed as a function of temperature would be most desirable. It is likely that these experiments will provide direct clues in understanding the anomalous behaviour of the impurity $H(T)$ documented for the case of a Co host.

5. Conclusion

In summary, we have shown from ^{119}Sn Mössbauer measurements on well characterised samples of Pd_2MnSn, that although the temperature dependence of the magnetic field $H(T)$ scales with the host magnetisation $M(T)$, the isomer shift $\delta(T)$ and the recoil-free fraction $f(T)$ change anomalously for $T < T_C$. The physical origin of these anomalies is believed to be magnetically induced. In particular, the anomalous decrease in $\delta(T)$ for $T < T_C$ reflects an electron–magnon coupling that is mediated by phonons, while the large increase in $f(T)$ is suggestive of a magnon-induced hardening of phonons in the cubic $L2_1$ structure.

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