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Résumé. - Les facteurs de structure, le facteur de forme magnétique et la distribution spatiale de la densité d'aimantation dans le composé Pd_2MnSb ont été déterminés par des mesures de diffraction de neutrons polarisés faites sur le diffractomètre D3 de l'I.L.L. On observe un moment ferromagnétique important essentiellement localisé sur les sites ordonnés des Mn. Le facteur de forme magnétique est en bon accord avec celui calculé par Watson et Freeman pour les ions Mn^{++}. Un moment magnétique équivalent mais de signe opposé est observé sur le petit nombre d'atomes Mn occupant une position desordonnée (sites Sb). On n'observe pas de moment mesurable sur les sites du Pd.

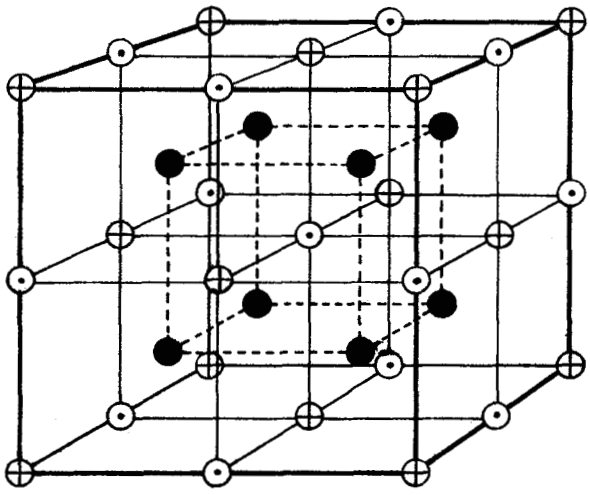
Abstract. - The structure factors, magnetic form factor and the spatial distribution of the magnetisation density in Pd_2MnSb have been studied by polarised neutron diffraction using the D3 diffractometer at I.L.L. The large ferromagnetic moment observed is essentially localised at the ordered Mn sites and the magnetic form factor is in good agreement with that for Mn^{++} ions calculated by Watson and Freeman. An equivalent but negative moment is observed on the small proportion of disordered Mn atoms occupying Sb sites. No measurable moment was observed on the Pd sites.

1. Introduction. - The Heusler alloys are ternary intermetallic compounds with the $L2_1$ structure indicated in figure 1. They are an interesting series for magnetic investigation because they offer an opportunity for determining the effects of interatomic distance, atomic arrangement and electron concentration on the occurence and type of magnetic order in 3d metallic systems.

The original Heusler alloys were all ferromagnetic and based on the composition Cu_2MnZ, where Z is an sp element in sub-group 3,4 or 5. Later a number of isostructural alloys, in which nickel or cobalt was substituted for copper, were also discovered. The latter however, from a theoretical viewpoint, suffer from the complication of containing a constituent that in its elemental state is strongly ferromagnetic.

In 1960, in a search for further examples of Heusler type alloys, Hames [1] reported two new intermetallic compounds containing palladium, PdMnSb and Pd_2MnSb. The former was a strong ferromagnet but the latter responded only feebly to an external magnetic field at room temperature. Hames tentatively concluded, from X-ray powder photographs, that Pd_2MnSb had the Heusler structure and PdMnSb the $C1_b$ structure. The latter structure is similar to the $L2_1$ but with alternate former Pd sites replaced by ordered vacancies. Webster and Tebble [2] made detailed magnetic, X-ray and neutron diffraction measurements on polycrystalline samples of Pd_2MnSb. They showed that at low temperatures the material was indeed ferromagnetic with a Curie temperature 247 K and a saturation moment 4.40 μ_B. The combined X-ray and neutron diffraction data confirmed that the constituents were highly ordered in the Heusler structure. The lattice parameter was measured as 6.42 Å giving a nearest Mn-Mn separation of 4.5 A, the largest then known in Heusler alloys. The neutron data also indicated that to within the limits of measurement, which was approximately ± 0.2 μ_B, the entire moment appeared to be associated with the Mn sites.

HEUSLER ($L2_1$) STRUCTURE OF Pd_2MnSb



Pd Mn Pd Sb

$$F^2(111) = 16(Mn - Sb)^2$$

$$F^2(200) = 16|2Pd - (Mn + Sb)|^2$$

$$F^2(200) = 16|2Pd + (Mn + Sb)|^2$$

Fig. 1

The Mn-Mn separation in Heusler alloys in general, and Pd_2MnSb in particular, are so large that direct d-d overlap is negligible and the magnetic coupling must be indirect via the conduction electrons or via a superexchange. For a particular theoretical interpretation to be soundly based, accurate measurements of the spin density distribution are required.

Ishikawa et al. [3], using the D5 polarised neutron spectrometer at the ILL, made measurements on a single crystal close to the composition Pd_2MnSn. Although the experimental conditions were not optimal they were able to conclude that the moment was largely localised at the Mn sites and that the form factor was adequately described by the Mn^{++} ionic form factor calculated by Watson and Freeman [4]. They also concluded that the Pd sites had a small positive polarisation $0.1 \pm 0.05\ \mu_B$ and that there was possibly a small negative polarisation at the Sn sites $\lesssim 0.1\ \mu_B$. However, both these moments were close to the limits of accuracy of the measurements.

Results are presented here of a polarised neutron investigation of a single crystal of Pd_2MnSb.

2. Experimental details. - A single crystal ingot of the intermetallic compound Pd_2MnSb was grown from the melt, by Perrier de la Bathie at C.N.R.S., Grenoble, using the Bridgman technique. A pillar shaped specimen, of dimensions 5x5x10 mm, was cut out such that a $\langle 1\bar{1}0 \rangle$ zone axis was along the long axis of the pillar. The crystal was then mounted on an aluminium pin and inserted at the centre of a 4.8 Tesla asymmetric split pair superconducting magnet located on the D3 polarised neutron diffractometer at ILL, Grenoble. The temperature was maintained at 30 K and the incident wavelength was 0.9 Å.

Flipping ratio measurements, R, were measured for all reflections hkℓ out to $(\sin\theta)/\lambda = 0.94\ Å^{-1}$ in the zero and first layers. In addition to the polarisation ratio measurements, measurements were made of a series of integrated intensities of independent reflections in order to determine the degree of chemical order in the sample.

3. Results and discussions. - After a least squares refinement the following scattering amplitudes were obtained for the three atomic sites

$$b_{Pd} = 0.65 \pm 0.04 \quad cm^{-1}$$
$$b_{Mn} = -0.31 \pm 0.02 \quad cm^{-1}$$
$$b_{Sb} = 0.50 \pm 0.03 \quad cm^{-1}$$

with an R factor of nuclear refinement 7%.

The average site moments, obtained from the flipping ratio measurements were

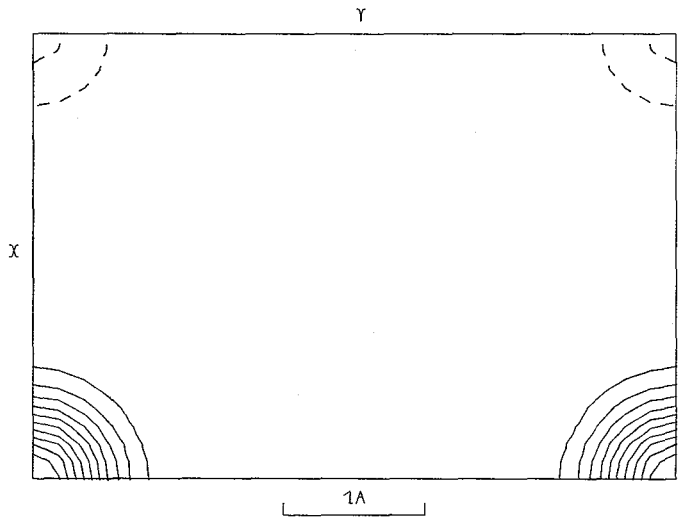
$$\mu_{Pd} = 0.02 \pm 0.01 \quad \mu_B$$
$$\mu_{Mn} = 4.58 \pm 0.07 \quad \mu_B$$
$$\mu_{Sb} = -0.18 \pm 0.01 \quad \mu_B$$

with an R factor of magnetic refinement 4%.

A Fourier section at the origin in the (110) plane of the measured magnetisation density is shown in figure 2(a). Figure 2(b) shows the equivalent calculated section assuming a Clementi wave function [5] appropriate to a Mn^{++} ion in the dipole approximation. Figure 3(a) shows the difference map $F_{obs} - F_{calc}$, scaled up by a factor of 10. Figure 3(b) shows an equivalent difference map using a model in which the appropriate Sb wave function was used for the Sb sites.

The measured nuclear scattering amplitudes for the 3 sites indicate that the palladium is highly ordered but that there is 4.6 ± 0.7% Mn-Sb disorder on the other two sites. The spin density maps show that the large ferromagnetic moment is localised at the ordered Mn sites and is essentially spherically symmetric. There is also a small negative moment at the 'Sb' sites. However, the difference maps clearly show that the negative density is more extended than that calculated using the Sb

PD2MNSB MAGNETIC DENSITY TEMP = 30K

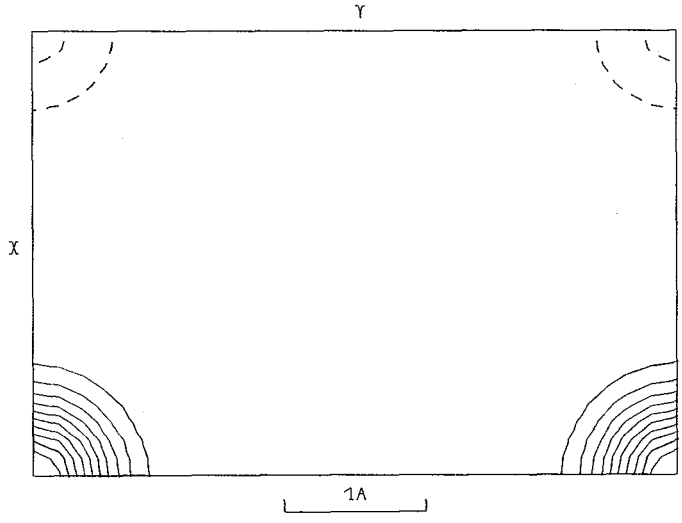


FOURIER SECTION AT			0		ON	100010000		
X PARALLEL TO	0	0	1	FROM	0	TO	0.5	
Y PARALLEL TO	1	1	0	FROM	0	TO	0.5	
COEFFICIENTS ARE		FOBS		MULTIPLIED BY			100	
AND AVERAGED OVER A CUBE OF EDGE			0.5					

Fig. 2(a)

CONTOURS
50
100
150
200
250
300
350
400
450
500
450
450
-50
-25

PD2MNSB MAGNETIC DENSITY TEMP = 30K



FOURIER SECTION AT			0		ON	100010000		
X PARALLEL TO	0	0	1	FROM	0	TO	0.5	
Y PARALLEL TO	1	1	0	FROM	0	TO	0.5	
COEFFICIENTS ARE		FCALC		MULTIPLIED BY			100	
AND AVERAGED OVER A CUBE OF EDGE			0.5					

Fig. 2(b)

CONTOURS
50
100
150
200
250
300
350
400
450
500
450
450
-50
-25

PD2MNSB MAGNETIC DENSITY TEMP = 30K

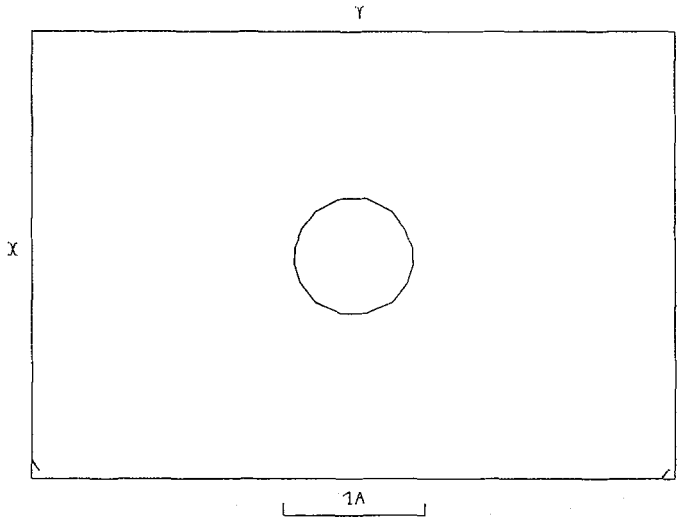


Fig. 3(a)

CONTOURS
50
25

FOURIER SECTION AT			0		ON	100010000		
X PARALLEL TO	0	0	1	FROM	0	TO	0.5	
Y PARALLEL TO	1	1	0	FROM	0	TO	0.5	
COEFFICIENTS ARE FOBS-FCALC MULTIPLIED BY 1000								
AND AVERAGED OVER A CUBE OF EDGE 0.5								

PD2MNSB MAGNETIC DENSITY TEMP = 30K

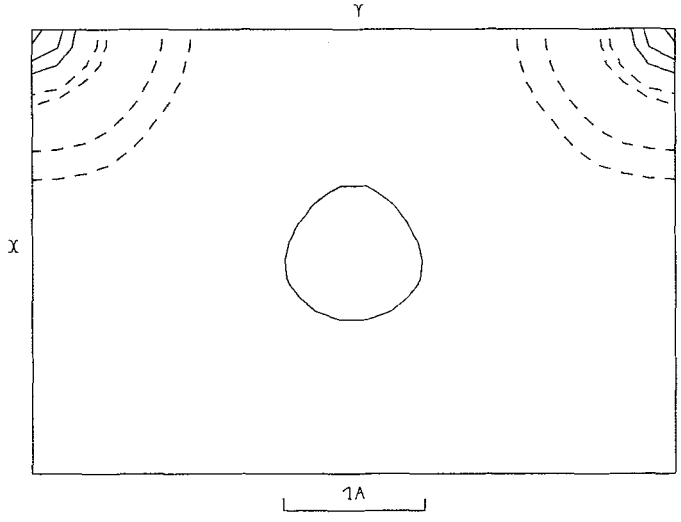


Fig. 3(b)

CONTOURS
50
100
150
-50
-25

FOURIER SECTION AT			0		ON	100010000		
X PARALLEL TO	0	0	1	FROM	0	TO	0.5	
Y PARALLEL TO	1	1	0	FROM	0	TO	0.5	
COEFFICIENTS ARE FOBS-FCALC MULTIPLIED BY 1000								
AND AVERAGED OVER A CUBE OF EDGE 0.5								

wave functions, but is well represented by that predicted using the Mn wave functions. Additionally, magnitude and sign are exactly what would be expected for 4% Mn occupancy of the 'Sb' sites, with a moment of 4.58 μ_B aligned antiparallel to the moment on the ordered Mn site. This is in agreement with the observations of the Le Dang Khoi et al. [6] from hyperfine field measurements, that in general Mn at the disordered site has a similar moment to the Mn on the regular site but with opposite sign.

Gyromagnetic ratios were determined using the dipole approximation for Mn at the regular and disordered sites. The values obtained were

$$g_{Mn} = 2.03 \pm 0.04$$

$$\text{and } g_{'Sb'} = 2.24 \pm 0.20$$

which, within the experimental error, do not differ from g = 2 indicating the absence of any significant orbital contribution. The fractions of electrons occupying orbitals of e_g symmetry were determined to be 0.45 ± 0.05 and 0.41 ± 0.1 for the regular and disordered sites respectively. For complete spherical symmetry the e_g occupation fraction should be 0.40.

In summary, the entire moment in Pd_2MnSb is localised on the Mn sites, is entirely spin in origin and is spherically symmetric. Any Mn atoms occupying 'Sb' sites are aligned antiparallel to the Mn site moments.

Ishikawa et al. [3] pointed out that Pd_2MnSn, when cooled, was a better polariser than Cu_2MnAl. Pd_2MnSb has a slightly greater moment than Pd_2MnSn and polarises just as well but at a higher temperature. The series $Pd_{2-x}MnSb$, for different values of x in the range $0 < x < 1$, can be made to polarise on the (111), (002), (220) or (222) reflections at temperatures between 100 and 300 K [7].

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