

ELECTRONIC STRUCTURE, MAGNETISM AND CURIE TEMPERATURES IN Fe, Co AND Ni

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Self-consistent para and ferromagnetic LMTO energy band results are presented for Fe (bcc structure), Co (hcp and fcc structure) and Ni (fcc structure) at different lattice constants, using local (spin) density formalism. The stability of the ferromagnetic states is predicted both from Stoner model and spin-polarized results. It is found that thermal broadening of the ($T = 0$) density-of-state functions, in addition to the Fermi smearing, is important to obtain reasonable values of the Curie temperatures when derived in the Stoner-sense. Increased broadening is required near T_c , as inferred from $T = 0$ results for the electron-phonon coupling. In Fe and Co, additional broadening may originate from relatively strong spin-phonon coupling. Cobalt under pressure, if stable in the fcc phase, is expected to show re-entrant magnetism.

1. Introduction

It is generally accepted that band theory using local density formalism provides a good description of itinerant spin magnetism at temperature $T = 0$. Thus the magnetic moments, m , in the ferromagnetic metals Fe, Co and Ni are calculated very near the measured values [1–3], but examples among compounds can also be found [4,5]. With regard to the exchange splitting, ξ , some disagreement arises when compared with that is found from angular resolved photoemission, at least for Ni [6–8]. The experimental exchange splitting is smaller than that calculated. In Ni, the value of ξ can decrease considerably without doing much to the band value of m , since the majority d-band is completely filled. Furthermore, photoemission identifies an exchange splitting at finite temperatures even above the Curie temperature, T_c [7,8]. This seems in contradiction with the Stoner approach of explaining the onset of itinerant band magnetism. In fact, paramagnetic density-of-state (DOS) obtained from band theory combined with Fermi-smearing gives much too high T_c s, by about factors of 5 [9,10]. As an alternative to the Stoner model at finite T , fluctuation of localized moments has been put forward as a more realistic model for

the observed behaviour. Strong support for this model is found from neutron diffraction, where indeed local moments correlated over some lattice spacings are observed above T_c in Fe and Ni [11].

Recently Pickett [12] has shown the importance of thermal broadening, entering via electron-phonon interaction and impurity broadening on various low temperature properties such as susceptibility, specific heat and superconducting transition temperature. Inclusion of only the temperature dependent Fermi function is inadequate to explain the low T properties of Nb_3Sn [12]. Although the temperature range for T_c in the three metals Fe, Co and Ni is high and is expected to give additional broadening effects than can be obtained from low T electron-phonon coupling, we will try to estimate the broadening effects in a simple approach. One of the main conclusions of this work is that with realistic values of the broadening parameter given in terms of an electron-phonon plus spin-fluctuation parameter λ , the Stoner criteria for determining T_c works quite well. This support for the Stoner model does not preclude fluctuations. Rather, the Stoner condition for the onset of magnetism has to be interpreted in the average sense. The time scale of the thermal lattice vibrations is much longer than the electron time

scale, which leads, in a given instant, to a distorted lattice without long range periodicity. The electron mean free path is shortened, leading to an uncertainty of its momentum k and associated energy E_k . Locally at a given time, the order can be large enough for the electrons to sense the ordinary long range DOS and a local magnetisation can be built up. The behaviour would be similar to a system with frozen disorder, such as with defects or impurities, creating a spin-glass structure with regions of varying magnetization.

The magnetization in Fe is larger than in Ni and Co and some other relevant differences are found between the three metals. But we believe that they are fundamentally similar and that even Fe is to a good approximation an itinerant band ferromagnet. The electronic structures are analysed and the results are presented for para and ferromagnetic states, T_c -estimates, magnetic moments, Stoner parameters, electron-phonon coupling and their variations with pressure.

2. Method

The electronic structures have been calculated using the Linear Muffin-Tin Orbital band method (LMTO) [13,14]. The paramagnetic potential is of the local density type of ref. [15] and for the spin polarized calculations we have added the local spin density functional of ref. [16]. The basis-set includes s, p, d and f for all atoms, with one additional l state in the three centre terms. Final bandstructures are given in 506 k points in the irreducible Brillouin-zone (IBZ) for Fe of bcc structure, in 385 k points in the IBZ for Co of hcp structure and in 505 k points in the IBZ for Ni of fcc structure. Density-of-state functions are determined using tetrahedron k point integration. Other details of the band calculation and the subsequent derivation of pressure, Stoner parameter and electron-phonon coupling have been published earlier [3,14].

For studying the high temperature fcc phase of Co, we added a set of calculations similar to the Ni fcc phase. The choice of lattice parameters was such that the atomic volume in the fcc phase was kept equal to the volumes chosen for the hcp

calculations. This made the self-consistent procedure simpler and allowed for exact comparison between the two structures.

3. Band structures and calculated pressures

The para and ferromagnetic band structures of Fe and Ni in ref. [1] and of Ni in refs. [2] and [3] are not very different from those found here. The calculation for Co in ref. [1] was for an assumed fcc lattice and our results for the real hcp structure show some essential differences compared to the fcc results [1]. The Co hcp band structure was studied earlier [17], but we are not aware of any recent spin-polarized local density calculation. Therefore, we show the bandstructure only for hcp Co. In fig. 1 is shown the DOS and in fig. 2 the bandstructure, while we refer to the literature for inspection of the detailed band structure of Fe and Ni [1–3]. Our exchange splittings differ somewhat

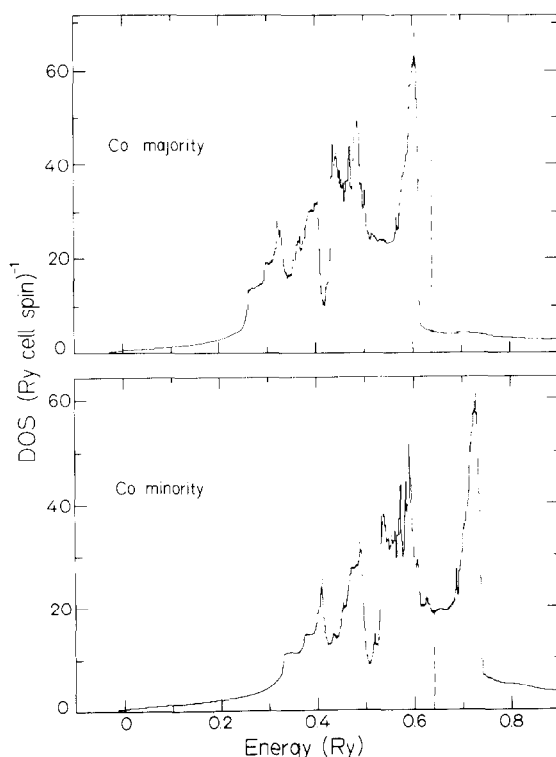


Fig. 1. Density of states for ferromagnetic cobalt in hcp structure.

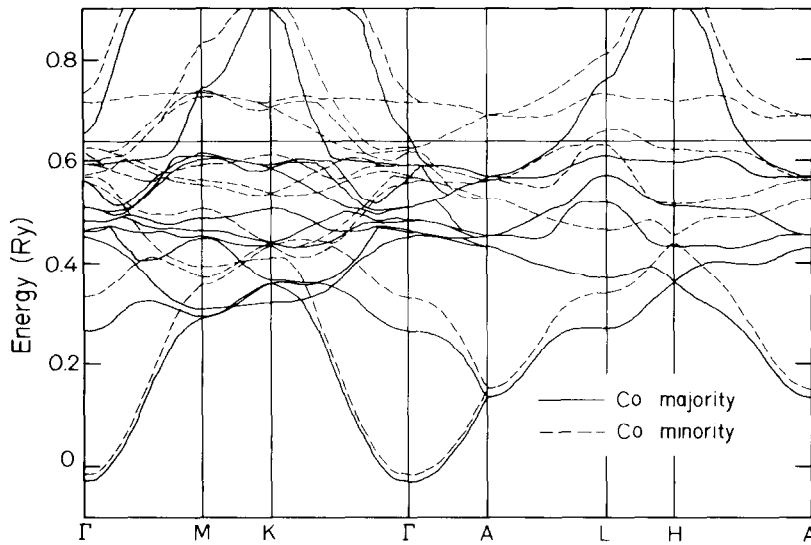


Fig. 2. Ferromagnetic bandstructure for hcp cobalt. Full lines are the majority bands, broken lines the minority bands.

Table 1

Majority and minority energies at symmetry points in mRy relative to the zero potential. These values are calculated using the experimental lattice constants. Degeneracies are indicated within brackets

Fe (bcc), $E_F = 610$.

	Γ			H		N		P		
	-18	14	(2)	269	381	254	352	(3)	375	491
(3)	443	595	(3)	614	786	366	504	(2)	563	731
(2)	546	708				545	661			
						561	708			
						631	727			
						633	808			

Co (hcp), $E_F = 640$.

	Γ		M		K		A		L		H					
(2)	-30	-18	291	358		323	408	(2)	134	151	(2)	271	340	(2)	363	440
	267	333	295	371	(2)	359	434	(2)	431	526	(2)	371	464	(2)	364	452
	451	558	310	391		367	435	(4)	454	561	(2)	519	632	(2)	433	517
	460	568	447	506	(2)	438	436	(4)	570	690	(2)	572	663	(2)	511	623
	464	572	452	554		507	613				(2)	610	735	(2)	598	723
	483	594	463	562	(2)	586	707				(2)	759	810			
	508	616	488	593		593	715									
	509	624	604	727												
	566	625	610	734												
	593	716	615	740												
652	733	745	835													

Ni (fcc), $E_F = 558$.

Γ			X		W			L		K		
	-115	-111	205	234		272	303		205	231	259	291
(3)	387	429	256	291	(2)	339	374	(2)	381	423	288	321
(2)	464	509	517	564		458	502	(2)	520	567	410	446
			(2)	535	582	535	583		526	530	475	520
				739	743						516	563

from the earlier calculations and in table 1 we show the values of ξ , at some symmetry points. The values for ξ , in Ni as well as the moment m , performed earlier using essentially the same LMTO approach, were slightly smaller [3]. However, the present LMTO calculation includes f states in the basis-set and uses 506 instead of 89 k points in the IBZ.

Moruzzi et al. [1] presented their band results, not for the experimental lattice constant but at a slightly reduced lattice constant, a , where the local density pressure (P) is zero. Also in our cases, we find quite a large negative pressure at the experimental a , see table 2. This discrepancy, corresponding to $\frac{1}{2}$ –1% difference in a , may well be a result of the local density approximation. Many properties, especially those related to the DOS at the Fermi energy E_F , depend sensitively on the lattice spacing. We present band results for several different lattice constants (of which one is the experimental) in table 2 and the variations of DOS at E_F , $N(E_F)$, with pressure is seen to be considerable. An extrapolation to $P = 0$ gives a reduction of $N(E_F)$ in the paramagnetic cases of 10–20% compared to when using the experimental lattice constants. However the ferromagnetic results (which are the realistic cases to compare with experiment) show smaller disagreement between

the results obtained at the experimental lattice constant and a lattice constant around which P is calculated to be zero. In other words, the errors in calculated pressures appear smaller, about $\frac{1}{2}$, when spin polarized potentials are used. The values of B , the bulk moduli, calculated as $-V\Delta P/\Delta V$, are almost the same using spin-polarized or paramagnetic pressure results. The paramagnetic values for B evaluated around $P = 0$ for Fe and Ni give almost a factor two too high values. The inconsistency between calculated P and B values is also evident from the fact that at experimental lattice constants, where the P values are too large and negative, the obtained B values agree well with experiment. (It should be noted that the calculated B values shown in table 2 are upper limits, since they are obtained from using the experimental and a reduced lattice constant. A correct evaluation would also need P results at an expanded lattice constant, in order to get the proper V derivative, and the results would agree better with experiment.) This behaviour is not due to lack of convergence, as we estimate such “error bars” to be 10–20 kBar in P , leading to errors in B of about 15%.

The magnetic moments, m , are in good agreement with experimental values for all three compounds if the experimental lattice constants are

Table 2

Paramagnetic and ferromagnetic band results for the DOS at E_F , $N(E_F)$ in units of states per Ry and atom, pressure and bulk moduli in Mbar for the three metals. The factor 2 for the paramagnetic $N(E_F)$ values are for the two spins. The bulk moduli are taken as linear differences around the average lattice constant. Experimental lattice constants (marked with an asterisk) and bulk moduli (1.68 for Fe, 1.91 for Co and 1.86 for Ni) are given in ref. [23]

	Lattice constant [au]	Paramagnetic			Ferromagnetic		
		$N(E_F)$ [Ry · atom] ⁻¹	Pressure [Mbar]	Bulk modulus [Mbar]	$N(E)$ [Ry · atom] ⁻¹	Pressure [Mbar]	Bulk modulus [Mbar]
					Majority	Minority	
Fe (bcc)	5.41 *	2 × 26.1	-0.42		11.9	3.5	-0.25
	5.16	2 × 21.4	-0.14	1.9	9.9	4.3	0.06
	5.06	2 × 19.8	0.07	3.4	-	-	-
Co (hcp)	4.69 *	2 × 20.1	-0.30		2.3	9.0	-0.19
	4.58	2 × 18.0	-0.15	2.1	2.4	8.7	-0.03
Co (fcc)	6.617	2 × 15.2	-0.31		2.1	15.5	-0.18
	6.462	2 × 13.5	-0.16	2.1	2.1	14.6	-0.02
Ni (fcc)	6.64 *	2 × 29.1	-0.23		2.3	22.4	-0.22
	6.50	2 × 27.0	-0.10	2.0	2.3	20.5	-0.08
	6.40	2 × 25.6	0.02	2.7			

used, while at $P=0$, values of m are reduced $\approx 1/10$. Also the hyperfine fields, H , although less well converged than the moments, seem in good agreement with experimental values at the experimental lattice constants, except in Ni. The H and m results, with their differences taken for pressure derivatives, are shown in table 3. The results, especially for H , differ from the results of Janak [18] based on the band results at reduced lattice constants [1]. We estimate our moments to be converged to less than 3%, while for H , the convergence may be achieved to only about 10%.

To summarize the discussion about the choice of lattice constants, it seems that most properties, except the pressure itself, show best agreement with experiment at the experimental lattice constant.

It is important to note that the spin polarized results cannot be modeled by rigidly shifting the paramagnetic band structures with an appropriate exchange splitting ξ . On a coarse scale the two spin bandstructures look similar, but the details can be very different. This can be seen for the Co bands and DOS functions. The differences between the two spins are even larger for Fe, while in Ni the differences are relatively small. Therefore we find larger differences for larger moments. In general the exchange splitting is zero or even reversed for s bands [19], which can be inspected at the lower part of the band structure. The resulting

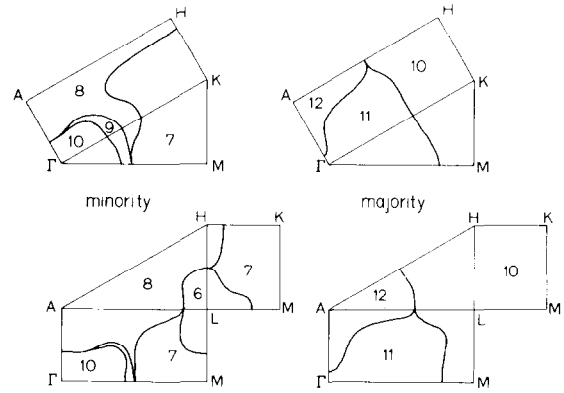


Fig. 3. Majority and minority Fermi surface structures for hcp cobalt. The numbers refer to the number of occupied bands in each region.

effects induced in the self-consistent potential differences between the spins are shown in fig. 4 for Ni. A rigid band splitting would give a constant potential splitting, equal to ξ , but as seen for Ni, the potential difference has a localized maximum about 75 mRy near the peak of the 3d wave function. Further out in the atomic cell, a reversed potential difference is induced and is largest at the boundary (7 mRy). The 4s electrons have their largest amplitude in the outer regions, which leads to a negative spin polarization in the interstitial volume. The same behaviour is seen also for Co and Fe, but with larger amplitudes. In Fe the spin

Table 3

Calculated moments, m , and hyperfine fields, H , and their pressure differences. The hyperfine fields are less well converged than the moments and can to some extent explain the poor values for $\Delta \ln H / \Delta P$. Experimental values are quoted from refs. [1] and [8]. However, the $T = 0$, measured values of m quoted in refs. [23] and [24] have been corrected using the gyromagnetic ratios of ref. [24] to obtain the m -experimental appropriate for comparison with spin-polarized, calculated results

	Lattice constant [au]	Magnetic moment m [μ_B /atom]		Hyperfine field H [kG]		$\frac{\Delta \ln m}{\Delta P}$ [Mbar] $^{-1}$		$\frac{\Delta \ln H}{\Delta P}$ [Mbar] $^{-1}$	
		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Fe (bcc)	5.41	2.26	2.1	-340	-339	-0.38	-0.32	-0.51	-0.17
	5.16	2.01	-	-288	-	-	-	-	-
Co (hcp)	4.69	1.55	1.6	-291	-	-0.25	-	-0.29	-
	4.58	1.49	-	-277	-	-	-	-	-
Co (fcc)	6.617	1.58	-	-283	-217	-0.23	-0.22	-0.11	0.60
	6.462	1.52	-	-278	-	-	-	-	-
Ni (fcc)	6.64	0.60	0.56	-98	-75	-0.24	-0.30	-0.07	0.81
	6.50	0.58	-	-99	-	-	-	-	-

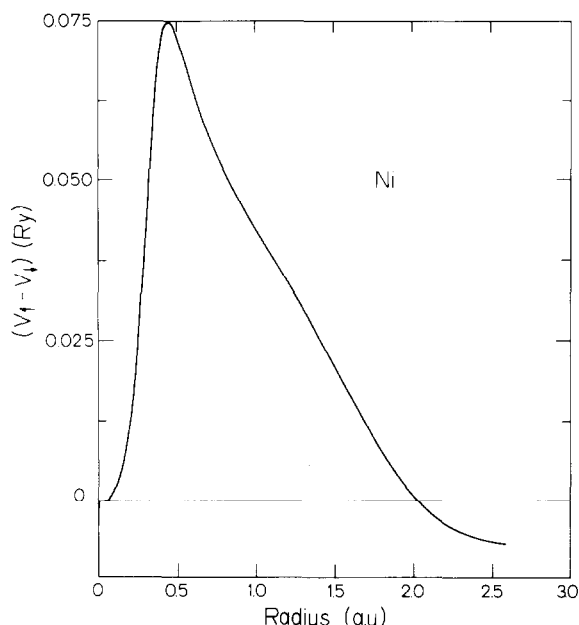


Fig. 4. Difference in the self consistent majority and minority potentials within the Wigner-Seitz sphere for Ni. The peak value (75 mRy) is about twice the average exchange splitting.

splitting is so large that the difference between the two spin 3d wave functions at E_F is important. Thus, the minority states are notably more delocalized than the majority states. Otherwise no principle difference is found between the three metals. It is only the amplitude of the spin-polarization which is different. The results for m and H and their variation with pressure as obtained from the spin-polarized calculations are summarized in table 3.

Next, we turn to the paramagnetic results, which we will use for a Stoner model and a derivation of the Curie temperature. Here the problem is that we want to describe the systems above or near T_c with band structure results evaluated for $T = 0$. The lattice constants are expanded, but the expansion is a result of increased pressure, induced by the delocalization of the wavefunctions etc., i.e. due to several complex processes which are difficult to predict. In order to choose a lattice constant for analyzing the "paramagnetic" states near T_c , we will use the pressure results as a guide. Spin polarized results using experimental lattice constants gave pressures of -250 , -190 and -220

kB for Fe, Co and Ni, respectively. Assuming similar "errors" for paramagnetic results, one finds at these pressures the approximate lattice constants 5.25 (Fe), 4.61 (Co) and 6.62 au (Ni), to be probable if the systems were prevented from developing ferromagnetic order at $T = 0$. For large T an internal pressure is generated, which could be modeled by the reduction of the lattice constants. Part of the pressure is released by lattice expansion, but quantitative estimates of the combined effects of elevated temperatures are uncertain. We have performed the paramagnetic band calculations using the same lattice constants as were used in the ferromagnetic calculations (which are close to those deduced above), but for the discussion in the next paragraphs concerning the effects of elevated temperatures on the calculated band structures, we note the uncertainty concerning the choice of lattice constants. The effects of temperatures near T_c , including effects of thermal disorder, will be considered in the next paragraph.

The DOS at E_F in the paramagnetic states shows a rapid decrease with pressure. This is because E_F falls on peaks in the DOS and with pressure the bandwidth increases and the height of the peak is rapidly decreased. But the position of the E_F relative to the 3d band peak is rather stable. In the ferromagnetic states the position of the E_F for the two bands moves slightly with pressure, while $N(E_F)$ is rather stable, since spin polarization caused the E_F to fall beside the high peaks in the DOS.

The differences in $N(E_F)$ in the para and ferromagnetic cases are very large. In Fe and Co, $N(E_F)$ is reduced more than two thirds, due to spin polarization. This is very different from the Co fcc results, where the reduction was found to be only about one third (cf. table 2).

At this point, we should compare the results for cobalt in the hcp and fcc phases. (The hcp phase is the low temperature phase, while at ≈ 400 K the stable phase is fcc.) All properties not depending on the DOS at E_F are very similar. Thus the calculated pressures are shifted about 20 kB independent of lattice volume or spin polarization, so that the fcc phase has the highest pressure and the slightly larger equilibrium lattice volume. The magnetic moment in the fcc phase is about $0.03\mu_B$

(2%) larger than the corresponding hcp phase. The small differences in m and P make small differences in total energy probable and a phase transition may occur already at low temperatures. However, we have not tested if the same was true also involving the bcc phase, or for Fe and Ni. A complete study of a possible phase transition would require total energy calculations for the two phases, which we have not performed here.

For properties related to the value of the DOS at E_F , there are large differences between two Co phases. These differences have significance for the electron-phonon coupling and Stoner parameter discussed later. The spin-polarized $N(E_F)$ values differ especially, due to the different shapes of the hcp and fcc DOS functions. The Fermi energy for the hcp minority band falls in a marked valley in the DOS, not present in the fcc DOS. Our results for the Co fcc phase agree well with that of ref. [1].

4. Electron-phonon coupling

The electron-phonon coupling has been calculated in the usual rigid-atomic-sphere approximation [20] and the phonon moments, ω^2 , are taken as $\frac{1}{2}\theta_D^2$, where θ_D is the experimental Debye temperature. No variation of θ_D with pressure is taken

into account. The results for para and ferromagnetic states are summarized in table 4. The "paramagnetic" specific heat derived from the obtained λ and $N(E_F)$ are well above measured values. The "ferromagnetic" specific heat, γ , calculated as $(\pi k^2/3)[N_\uparrow(E_F)(1 + \lambda_\uparrow) + N_\downarrow(E_F)(1 + \lambda_\downarrow)]$ are, as seen, considerably smaller than measured, especially for Fe and Co. This leaves space for processes like spin-fluctuations to contribute with a λ of the order $\frac{1}{2}$ or more. Such fluctuations would transfer electrons from one spin to the other, making the amplitude of the local moment very, and are most possible if the $N(E_F)$ of both spins are large and equal. In Ni the total $N(E_F)$ is quite large, but the ratio between the DOS of the spins is large, about 10. In Co and Fe the total $N(E_F)$ are not as large, but more equally distributed between the two spins. The theories of spin-fluctuations on λ are not directly transferable from paramagnetic to ferromagnetic systems and we have not tried quantitative estimates here.

An additional contribution may also come from the coupling between spin fluctuations and phonons. They may be of importance at large temperatures around T_c , where the fluctuations around zero average moment are strong. From the pressure results, one found differences in pressure between para and ferromagnetic states, namely

Table 4

Calculated Stoner factor \bar{S} electron-phonon coupling λ and electronic specific heat, γ , for para and ferromagnetic cases. Experimental data are taken from ref. [23]. The Debye temperatures used in the calculations of λ were Fe: 470 K, Co: 445 K and Ni: 450 K. Experimental values for γ are: Fe: 4.98, Co: (the low temperature phase is hcp) 4.73 and Ni: 7.02 mJ/mol·K². The decrease of \bar{S} with pressure is due to the decrease of the DOS at E_F . The parameter I (see text) increases slightly with pressure. The corresponding values for I at experimental lattice constants are: Fe: 33.7, Co (hcp): 35.5, Co (fcc): 34.8 and Ni 36.6 mRy

	Lattice constant [au]	Paramagnetic			Ferromagnetic		
		\bar{S}	λ	γ [mJ/mol·K ²]	γ		
					Majority	Minority	γ [mJ/mol·K ²]
Fe (bcc)	5.41	1.76	0.48	13.4	0.22	0.22	3.3
	5.16	1.46	0.74	—	0.35	0.42	3.4
	5.06	1.36	0.89	—	—	—	—
Co (hcp)	4.69	1.43	0.45	5.1	0.07	0.44	2.7
	4.58	1.28	0.51	—	0.08	0.54	2.8
Co (fcc)	6.617	1.05	0.39	—	0.05	0.70	—
	6.462	0.95	0.45	—	0.06	0.74	—
Ni (fcc)	6.64	2.13	0.26	12.7	0.06	0.32	5.6
	6.50	1.99	0.28	—	0.04	0.35	5.2
	6.40	1.90	0.28	—	—	—	—

170 kB for Fe, 110 kB for Co and rather small 15 kB for Ni. This translates into about $75 \text{ kB}/\mu_B$ for Fe and Co, while less $25 \text{ kB}/\mu_B$ for Ni. Or in terms of volume change per Bohr magneton one finds approximately 4% volume expansion per μ_B for Fe and Co. Thus, a local spin fluctuation provokes a local lattice instability, which in turn leads to increased disorder. The opposite development, where an induced lattice expansion carries along a spin enhancement, seems also feasible. These processes are probably important at high temperatures, but to estimate the effects into a quantitative parameter λ is a difficult task.

As can be seen in table 4, there is a rather important increase of the (paramagnetic) electron-phonon coupling with increasing pressure. The effect amounts to about 0.9 Mbar^{-1} for Fe, about 0.4 Mbar^{-1} for Co, but very little for Ni. (The Debye temperature is assumed constant.) The result is qualitatively the same from the spin-polarized results. This is somewhat surprising, since one usually identifies a large $N(E_F)$ with large λ . But for Co and in particular Fe, the λ goes up when $N(E_F)$ goes down with pressure. In Ni, $N(E_F)$ also decreases with pressure, while λ is rather constant. As the lattice becomes contracted, there is a relative delocalisation of the wave functions which enhances the contribution to λ . In Ni the effect of this “softening” is smaller, since E_F is near the top of the 3d band where the band is localized, i.e. the amplitude for the 3d wave function in the outer part of the atomic sphere is always near zero. Another example of the importance of contributions to λ which are not related to $N(E_F)$, can be seen for spin polarized Fe. The $N(E_F)$ differ by a factor of 3, while the two λ are equal for the two spins. The majority $N(E_F)$ is large, but the states at E_F are localized, while the delocalized minority states are soft and gives an important contribution to λ .

5. Stoner parameters and Curie temperatures

From the paramagnetic band results, one can calculate the Stoner enhancement parameter $S = \chi/\chi_0 = (1 - \bar{S})^{-1}$ [5,10,21]. For \bar{S} less than one, S is a measure of the magnetic susceptibility en-

hancement for paramagnets. If \bar{S} is larger than one, S goes through a singularity, indicating that the system spontaneously undergoes a magnetization. It is energetically favourable to form a magnetic state and the paramagnetic DOS do not describe the ground state. The parameter \bar{S} can be written $N(E_F)I$, where I is an exchange correlation integral. The obtained values for \bar{S} and I are given in table 4. As seen, magnetism is clearly predicted for all the three metals, while from \bar{S} itself one cannot predict the amplitude of the stable moment. The value for \bar{S} obtained from the Co calculations in fcc structure [1,21] was less than one. Here we obtain $\bar{S} = 1.05$, while for the hcp phase, \bar{S} is much larger, 1.43.

However, spin polarized calculations show a stable moment for fcc Co similar to that obtained here for hcp Co.

The values of \bar{S} all decrease with applied pressure. This mainly depends on the variations of $N(E_F)$, since I is rather increasing with pressure. The contribution to I is dominated by the 3d band, which is most localized. With pressure there is a relative delocalization, but since the volume decreases, one also finds no large effect on the total I .

To calculate the magnetic ordering temperature, T_c , we employ the formula

$$I \int_{-\infty}^{\infty} N_{\text{eff}}(E) \frac{df}{dE} dE = \bar{S}(T), \quad (1)$$

and seek the temperature at which $\bar{S}(T)$ is one. Here $f = f(E_F, E, T)$ is the Fermi function and $N_{\text{eff}}(E, T)$ is an effective DOS, where effects from thermal disorder are included. We use an expression for N_{eff} given by Klein et al. [22]:

$$N_{\text{eff}}(E, T) = \int_{-\infty}^{\infty} d\epsilon N(\epsilon) \frac{\Gamma/\pi}{(E - \epsilon)^2 + \Gamma^2}, \quad (2)$$

where the broadening parameter Γ is $\pi\lambda_{\text{tr}}k_B T$. The transport enhancement factor λ_{tr} is approximated with the electron-phonon coupling value λ calculated at $T = 0$. Although eq. (2) is justified for $T \gg \theta_D$ [22], one could expect additional broadening due to the temperature dependence of λ and due to spin-coupling effects as discussed earlier.

The results for different λ and lattice constants

Table 5

Curie temperatures at different lattice constants and different broadening parameters λ . Values for λ marked with an asterisk are the ($T = 0$) calculated values. Co (fcc) under pressure is predicted to lose long range magnetic order, or to become a re-entrant magnet at elevated temperatures (see text). Experimental values for the Curie temperatures are: Fe: 1043 K, Co (fcc): 1388 K and Ni: 627 K [23]

	Lattice constant [au]	λ	Curie temp. [K]
Fe	5.41	0	5800
		0.48 *	2750
		1.5	1160
	5.16	0	4800
		0.74 *	1650
		1.2	1120
	5.06	0	4200
		0.89 *	1210
		1.0	1100
Co (hcp)	4.69	0	3850
		0.45 *	1900
		0.75	1360
Co (fcc)	6.617	0	3450
		0.39 *	1620
		0.5	1410
	6.461	0	~1600
		0.45 *	—
Ni	6.64	0	2200
		0.26 *	1070
		0.5	670
	6.50	0	2100
		0.28 *	970
		0.5	650
	6.40	0	2000
		0.28 *	940
		0.5	620

are summarized in table 5. For no thermal broadening, $\lambda = 0$, one retrieves the well known T_c s that are about 5 times too large than experimental values in all three metals [9,10]. Using the λ s calculated in the previous paragraph, at the lattice constants, which by pressure arguments (discussed earlier) ought to be appropriate for zero-moment phases, one finds a large improvement of the calculated T_c s. They are now less than twice the experimental ones, or approximately (after interpolating in table 5 for the given lattice constants quoted in paragraph 3) Fe 1900 K, Co 1800 K and Ni 1000 K. Although \bar{S} at $T = 0$ is largest for Ni, it

has the lowest T_c . This is because the peak in the DOS near E_F is rather narrow and easily “washed out” by broadening due to the Fermi function and thermal disorder. In Fe, the DOS peak is not as high at E_F , but wider, so $\bar{S}(T)$ decreases rather slowly with increasing T .

Evidently, the electron-phonon coupling λ calculated at $T = 0$, are generally too small to obtain the experimental Curie temperatures, when used in eqs. (1) and (2). The required amplitudes of λ would be about 1.3 (Fe), 0.6 (Co) and 0.5 (Ni), or almost twice the calculated ones.

Various possible sources of additional broadening have been mentioned earlier. Large increase of λ with pressure and large spin-phonon coupling in Fe and Co are expected to increase the broadening effects at large T . In addition, Fe has a bcc to fcc phase transition at about 200 K above T_c , which may be associated with a phonon softening and increase of λ already at lower temperatures.

It is somewhat surprising to find the Curie temperatures of hcp and fcc Co rather similar, when their DOS at E_F and $T = 0$ Stoner parameter are quite different. However, this is only accidental. The behaviour of the magnetic ordering between the two phases are predicted to be very different. In fcc Co, the Fermi energy falls rather near a valley in the DOS, so that with a certain amount of broadening the effective DOS at E_F can increase. In hcp Co as well as in Fe and Ni, broadening will always decrease the effective DOS at E_F . In fig. 5 we show the behaviour for $\bar{S}(T)$ for the two cobalt phases. The behaviour for hcp Co is similar to Fe and Ni, i.e. a steady decrease of \bar{S} with increasing T . For fcc Co, $\bar{S}(T)$ first increases and then decreases when T goes up. For an applied pressure, one can expect (if the fcc phase can be stabilized down to $T = 0$) to find a case, where $\bar{S}(T)$ is below one at $T = 0$, i.e. paramagnetic. As T increases, $\bar{S}(T)$ will eventually be larger than one and cause long range magnetism. At even larger temperatures, the magnetism disappears as $\bar{S}(T)$ goes below one at the Curie temperature. Thus, this would be an example of re-entrant magnetism occurring within a certain temperature range.

For the temperature dependence of the magnetic moment below T_c , the mean field theory

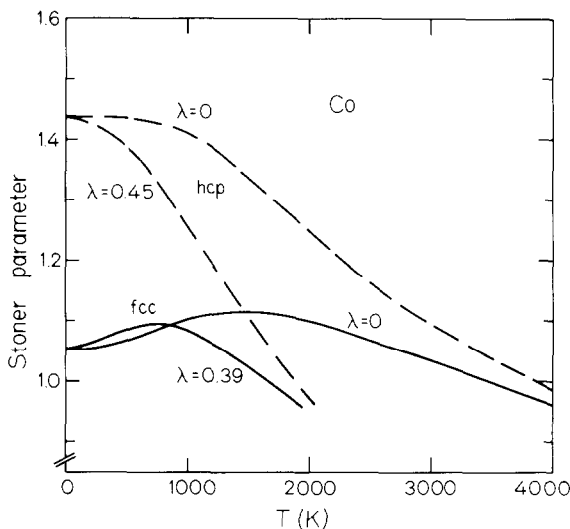


Fig. 5. The variation of the Stoner parameter with temperature for fcc (full lines) and hcp (broken lines) cobalt with and without thermal disorder. The behaviour for iron and nickel is qualitatively similar as for hcp Co. The effect of pressure is to shift the curves downwards.

gives the well known relation $m \sim \tanh(m/t)$, where m and t are the reduced moment and the temperature [23]. Quite good agreement with experiment is found for Ni, even though no information about $N(E)$ is included in the calculation. Thus the reduction of m with t does not appear to come from a continuous reduction of the exchange splitting, since one then would expect strong DOS related effects. Instead strong fluctuations and moments of various strengths are likely to be present, and additional broadening effects of the DOS do not give further clarification about the $m(t)$ behaviour.

6. Conclusion

The magnetic states in Fe, Co and Ni are well described from spin polarized calculations concerning the magnetic moment and hyperfine fields. In our study, the magnetic state in Ni is about 10% stronger than found experimentally, making it the least successful case. We find values for the exchange splitting roughly equal, as obtained in other studies using a different local density functional

[1,2], and for Ni there is a lack of agreement with experimental values obtained from photoelectron spectroscopy [8].

For the derivation of the Curie temperature, it is the paramagnetic DOS and the temperature dependence of the corresponding Stoner parameter, $\bar{S}(T)$, which is valid. At $T = T_c$, $\bar{S}(T)$ goes below one. As is well-known [9,10], including only Fermi smearing gives much too high T_c s. When the effects of thermal disorder are added, such as a broadening of the $T = 0$ DOS, one obtains much more realistic values of T_c . However, the broadening parameter has to be almost twice that obtained from $T = 0$ electron-phonon coupling, in order to obtain experimental T_c s. Qualitatively speaking this is not unexpected, since at relatively large Curie temperatures, a spin-phonon interaction as well as phonon softening is probable. The Stoner model has to be interpreted in an average sense as being the condition for long range order magnetism. This allows local spin fluctuations to interact with thermal disorder near T_c . It is important to note that broadening effects of the DOS in addition to Fermi-smearing [12] are important for temperature dependent properties derived from band theory. Further development of the theory for temperature effects on the band structure is needed, in order to take into account temperature and energy dependence of the broadening parameter for different bands.

Iron is the only one of the three metals that does not have a completely filled majority d-band, and the magnetic state in iron has therefore been expected to be different from those in Co and Ni. In this study we see no principal difference between the three metals. The same theories and methods have been employed for studying each metal and the agreements with various experiments are about equally good or bad for each one. The approach of itinerant band magnetism seems to work quite well for Co and Ni, as well as for Fe.

Cobalt, if stabilized in the fcc phase over all temperatures, could provide an interesting experimental test of the validity of the relation between $\bar{S}(T)$ and magnetic ordering. When a pressure is applied, $\bar{S}(0)$ goes below one and then increases with temperature until, at the Curie temperature, it once again goes below one. If the paramagnetic

state is not a metastable state, i.e. does not have a higher total energy than a competing ferromagnetic state, one would expect to observe long range magnetic ordering within a temperature range above $T = 0$. At even larger pressures, the upper and lower transition temperature will meet and the phase becomes a strongly enhanced paramagnet at all temperatures.

Note added in proof

Using obtained values of the bulk moduli and available values of the Grüneisen parameters, G (quoted in ref. [1]), one can estimate the increase of the Debye temperatures with pressure as $\theta(P) = \theta(0)(1 + GP/B)$. Including this in the calculations of $\lambda(P)$ one finds almost no variation for Fe and Co while negative $d\lambda/dp$ for Ni. Thus, our calculated values of the pressure variations of λ shown in table 4 and discussed in section 4, are too large, since the variation of $\langle\omega^2\rangle$ was assumed constant. We acknowledge discussions with Dr. Ö. Rapp who pointed out the importance of pressure variations of the Debye temperatures.

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