Itinerant magnetism of iron

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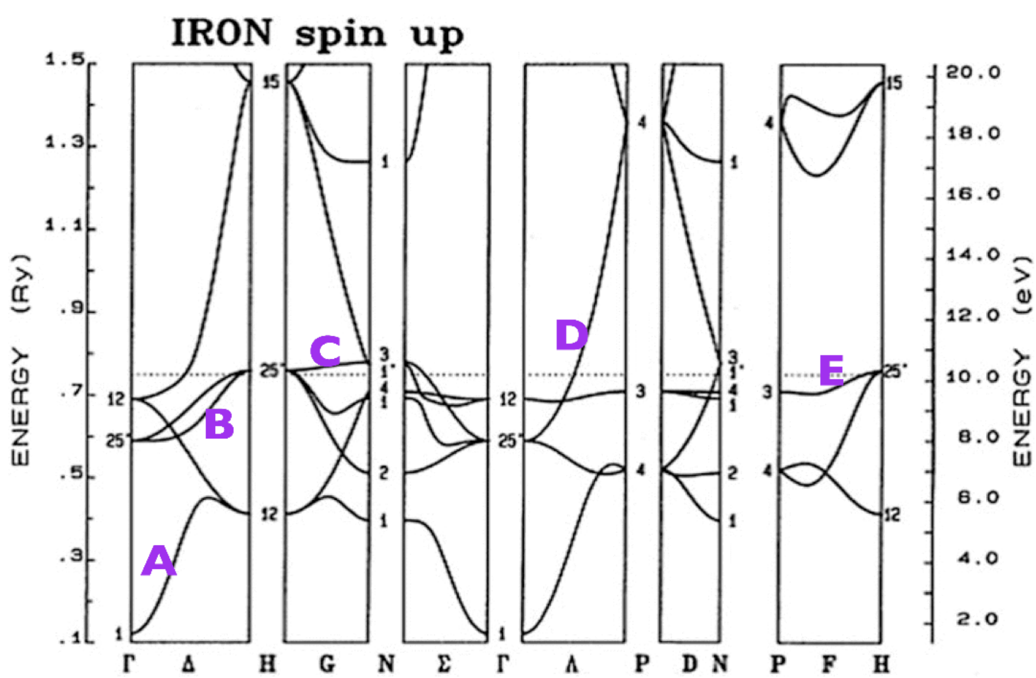
Localized *vs* itinerant character of metallic Fe electrons

The figure shows the band structure computed for majority-spin electrons of metallic iron.
Answer the following quizzes about the character of different energy bands.



Indicate in the correct answer to the following questions with a X at the beginning of the corresponding line.

Question 1: Referring to the figure above, which bands have mainly itinerant character?

* C and E
* D and A
* All of them because no band is perfectly flat.

Question 2: Referring to the figure above, which bands have mainly localized character?

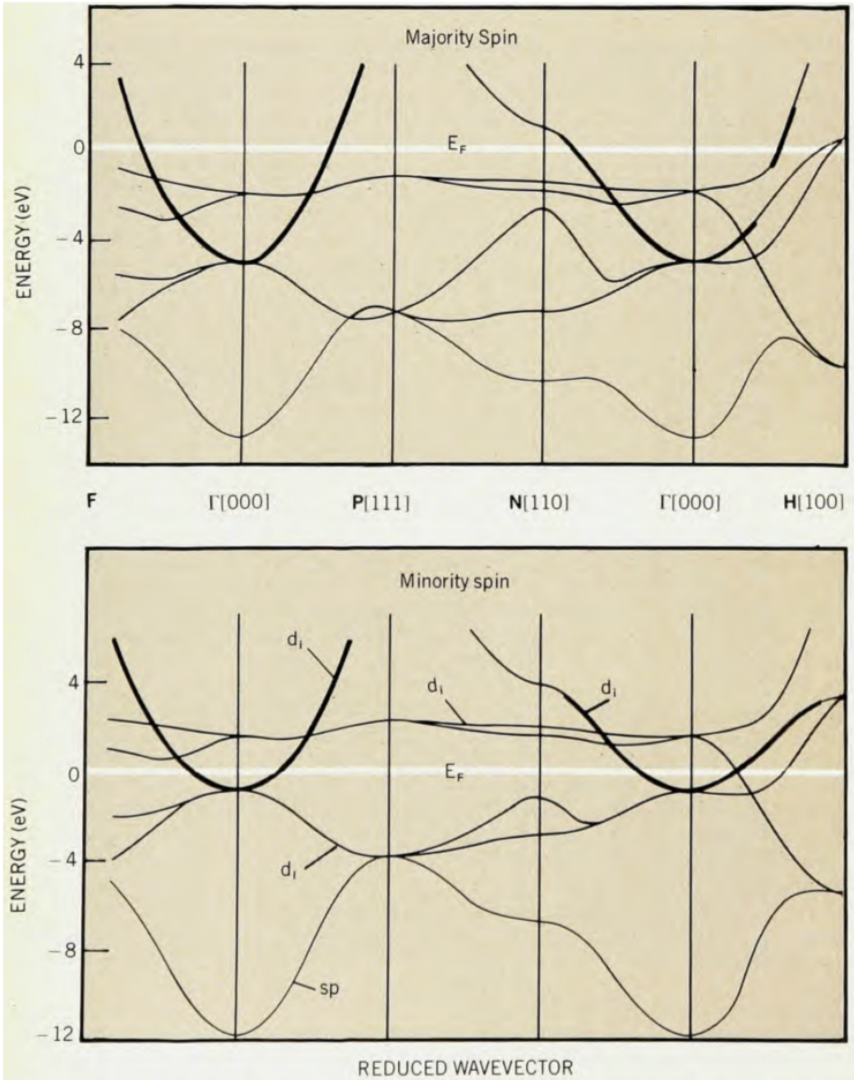
* C and E

* D and A
* It does not make sense to speak about localized state in a band model.

Question 3: Which band can be associated with the s electrons of the free ion?
* A
* B
* C
* D
* E
* None of them because free ion levels lose their meaning in a band model.

Magnetic moment of metallic Fe from band structure

The following figure compares the band structure of majority- and minority-spins electrons of Fe and is taken from the paper[1] of Mary B. Stearns “Why is iron magnetic?”(see file “./CourseLibrary/Articles/Stearns_Physics-today_1978.pdf”).



Referring to band structure of majority-spin electrons we shall indicate with $n^{\uparrow}$ the number of d$_{loc}$ bands, i.e., with dominant localized character, that lie below the Fermi level. We shall use the notation $n^{\downarrow}$ to indicate the same quantity for the minority-spin electrons.

Question Consistently with the two band structures of Fe shown above, what are the values $n^{\uparrow}$ and $n^{\downarrow}$?

- $n^{\uparrow} = 3$ and $n^{\downarrow} = 3$
- $n^{\uparrow} = 5$ and $n^{\downarrow} = 1$
- $n^{\uparrow} = 4$ and $n^{\downarrow} = 2$

1. Based on the answer to the previous question, estimate the magnetic moment contributed by localized d$_{loc}$ orbitals of metallic Fe (in the solid state) using the formula

$$\mu_{loc} = \frac{1}{2} g \left(n^{\uparrow} - n^{\downarrow}\right) \mu_{\rm B}$$

(assume $g = 2$). Is this contribution μ_{loc} larger or smaller than the magnetic moment μ_{O_h} of Fe^{2+} high-spin in an octahedral field of ligands (estimated in the question assignment **04-week-assignment.Rmd**)?

Answer

WRITE YOU ANSWER HERE

2. From the fraction of d$_{itin}$ electrons below the Fermi surface for the majority-spin and minority-spin bands, $f^{\uparrow}$ and $f^{\downarrow}$ respectively, estimate the contribution of the itinerant electrons to the magnetic moment of each Fe atom using the formula

$$\mu_{itin} = \frac{1}{2} g \left(f^{\uparrow} - f^{\downarrow}\right) \mu_{\rm B}$$

Hint: Assuming a parabolic dependence of the band energy on the wave vector k

$$E(d_{itin}) = \frac{\hbar^2}{2m^{\star}} k^2$$

look at the position of k_F for both minority and majority spin channels, with respect to the module of k at the end of the Brillouin zone, $k_{B.z.}$ and assume that the fractions $f^{\uparrow}$ and $f^{\downarrow}$ scale like the relative volume of the spheres with radii $k_F^{\uparrow}$ and $k_F^{\downarrow}$ with respect to the sphere with volume equal to the entire Brillouin zone. As a further simplification, you can limit yourself to consider the portion in between the points Γ and P of the Brillouin zone, i.e. just consider one value for $k_F^{\uparrow}$ and one value for $k_F^{\downarrow}$, respectively.

Answer

WRITE YOU ANSWER HERE

3. Compare the sum of μ_{loc} and μ_{itin} deduced at the points 1. and 2. with the experimental value $\mu_{\rm Fe} = 2.2\mu_{\rm B}$ for metallic Fe.

Answer

WRITE YOU ANSWER HERE

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1. Physics Today 31, 4, 34 (1978); https://doi.org/10.1063/1.2994993 (https://doi.org/10.1063/1.2994993)↩

Magnetic moment of metallic Fe from band structure

1. Based on the **correct** answer to the previous question, estimate the magnetic moment contributed by localized d_{loc} orbitals of metallic Fe (in the solid state) using the formula

$$\mu_{loc} = \frac{1}{2} g \left(n^{\uparrow} - n^{\downarrow} \right) \mu_{\mathrm{B}} \tag{1}$$

(assume $g = 2$). Is this contribution μ_{loc} larger or smaller than the magnetic moment μ_{O_h} of Fe^{2+} high-spin in an octahedral field of ligands (estimated in the assignment of 04-week)?

The correct answer is $n^{\uparrow} = 4$ and $n^{\downarrow} = 2$ which yields

$$\mu_{loc} = 2\mu_{\mathrm{B}} \tag{2}$$

Fe^{2+} high-spin in octahedral environment has $S_{O_h} = 2$ and $L_{O_h} = L' = 1$. In the assignment of 04-week we used the expression $p = \sqrt{4S_{O_h}(S_{O_h}+1) + L_{O_h}(L_{O_h}+1)}$ which yields $5.1\mu_{\mathrm{B}}$. Even assuming total quenching of the orbital momentum (i.e. setting $L_{O_h} = 0$) the magnetic moment would be $\mu_{O_h} = 4\mu_{\mathrm{B}}$, twice the value of $\mu_{loc} = 2\mu_{\mathrm{B}}$ computed above. Interestingly, the latter is the arithmetic average between the spin contribution to μ_{O_h} of the high- and low-spin configuration of Fe^{2+}.

2. From the fraction of d_{itin} electrons below the Fermi surface for the majority-spin and minority-spin bands, $f^{\uparrow}$ and $f^{\downarrow}$ respectively, estimate the contribution of the itinerant electrons to the magnetic moment of each Fe atom using the formula

$$\mu_{itin} = \frac{1}{2} g \left(f^{\uparrow} - f^{\downarrow} \right) \mu_{\mathrm{B}} \tag{3}$$

Hint: Assuming a parabolic dependence of the band energy on the wave vector k

$$E(d_{itin}) = \frac{\hbar^2}{2m^*} k^2 \tag{4}$$

look at the position of k_F for both minority and majority spin channels, with respect to the module of k at the end of the Brillouin zone, $k_{B.z.}$ and assume that the fractions $f^{\uparrow}$ and $f^{\downarrow}$ scale like the relative volume of the spheres with radii $k_F^\uparrow$ and $k_F^\downarrow$ with respect to the sphere with volume equal to the entire Brillouin zone. As a further simplification, you can limit yourself to consider the portion in between the points Γ and P of the Brillouin zone, i.e. just considering one value for $k_F^\uparrow$ and one value for $k_F^\downarrow$, respectively.

From visual inspection of the band structure for majority ($\uparrow$) and minority ($\downarrow$) spins one can estimate

$$\begin{aligned} k_F^\uparrow &= \frac{1.2}{2.2} k_{B.z.} \\ k_F^\downarrow &= \frac{0.5}{2.2} k_{B.z.} \end{aligned} \tag{5}$$

Therefore, the portion of volume of each itinerant band lying under the Fermi level w.r.t. the volume of the same band till the end of the Brillouin zone is

$$\begin{aligned} f^\uparrow &= \left(\frac{k_F^\uparrow}{k_{B.z.}}\right)^3 = \left(\frac{1.2}{2.2}\right)^3 = 0.162 \\ f^\downarrow &= \left(\frac{k_F^\downarrow}{k_{B.z.}}\right)^3 = \left(\frac{0.5}{2.2}\right)^3 = 1.17 \times 10^{-2} \end{aligned} \tag{6}$$

From this rough estimate one obtains

$$\mu_{itin} = \frac{1}{2} g \left(f^\uparrow - f^\downarrow\right) \mu_\mathrm{B} = 0.15 \mu_\mathrm{B} \tag{7}$$

3. Compare the sum of μ_{loc} and μ_{itin} deduced in the previous steps with the experimental value $\mu_\mathrm{Fe} = 2.2\mu_\mathrm{B}$ for metallic Fe.

   Adding up the contributions $\mu_{loc} = 2\mu_\mathrm{B}$ and $\mu_{itin} = 0.15\mu_\mathrm{B}$ deduced at the previous points, one obtains $\mu_{theo} = 2.15\mu_\mathrm{B}$, which – given the rough way in which the itinerant contribution was estimated – is in good agreement with the experimental value of $\mu_\mathrm{Fe} = 2.2\mu_\mathrm{B}$. Note that μ_{itin} is responsible for the non-integer contribution to the magnetic moment, in line with the Stoner-Wohlfarth-Slater model.