

## Magnetism in Iron at High Temperatures

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Magnetism in iron at high temperature is investigated by calculating the total electronic band-structure energy for four types of spin arrangements. A slow smooth spatial variation of spin direction costs relatively little energy and the atomic moment  $m$  is reduced only  $\sim 10\%$ . More rapid variations have considerably higher energy, which may explain the high degree of short-range order and small  $\delta m$  observed at  $T \approx T_C$ . Other aspects are also discussed.

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The magnetic properties of metallic iron at high temperature are still not fully understood. A large body of opinion<sup>1-8</sup> believes that magnetic disorder sets in as a result of the rotation of atomic moments  $\vec{m}_i$ . This leads to a Curie temperature  $T_C \sim v^2/W$  an order of magnitude lower than in simple Stoner<sup>9</sup> theory where  $T_C(\text{Stoner}) \sim v$  where  $W$  is the width of the electron energy bands and  $2v$  their exchange splitting. Above  $T_C$  iron<sup>10</sup> (and nickel<sup>11</sup>) appears to retain a remarkable amount of short-range order,<sup>1-4, 10</sup> well defined spin-wave excitations having been measured to  $1.4T_C$ . Quantitative understanding of this situation in terms of metallic electronic structure is still lacking though there have been significant recent theoretical advances.<sup>1-8</sup>

We have calculated the electronic structure and total energy  $U$  of Fe with various spin arrangements to investigate (a) to what degree the atomic magnetic moment is retained<sup>12</sup> when spins rotate; (b) the reason for the large short-range order<sup>10</sup> above  $T_C$  and its form; and (c) the magnitudes of the first-, second-, etc., neighbor couplings, among other aspects. We believe that these are the first *ab initio* calculations to throw light on the magnetic interactions in Fe beyond a nearest-neighbor picture and on the short-range order above  $T_C$ .

Our tight-binding model has five  $d$  orbitals with or without an  $s$  orbital to represent somewhat crudely the  $sp$  band. The hopping parameters are taken from Eqs. (9) and (10) of Pettifor<sup>13</sup> with  $W_d = 0.46$  Ry. As in Ref. 5, the exchange potential<sup>9</sup>  $V_{\text{ex}} = \pm v_i$  on atom  $i$  acts on each  $d$  orbital with down (up) spin, with the  $\pm$  sign defined with respect to the *local*<sup>1</sup> direction  $\hat{m}_i$  of the magnetic moment  $\vec{m}_i$  on atom  $i$ . The *directions*  $\hat{m}_i$  are imposed in calculating the electronic structure for any desired spin arrangement. The magnitudes  $v_i$  and corresponding  $m_i$  have to be determined self-consistently<sup>9</sup> by  $2v_i = Im_i$  in terms of the

Stoner intra-atomic exchange interaction  $I = 0.07$  Ry taken from Gunnarsson.<sup>14</sup> The time variation of the spin arrangement is ignored as slow compared with electronic motion, and the temperature  $T \sim T_C$  assumed sufficiently below  $T_C$  (Stoner) for single-particle excitations<sup>9</sup> to be neglected. The total energy  $U$  is  $U_1$  (the sum of occupied one-electron energies) plus the correction  $\sum_i v_i^2/I$  for double-counting exchange. The recursion method<sup>15</sup> applied to a large cluster of 700 atoms (8000 spin orbitals) allows us to calculate the local density of states near the cluster center and hence  $U$  for an arbitrary arrangement of spin directions, regular or random.

Stoner-type theory has given a fairly successful account of the ground-state properties of ferromagnetic metals such as Fermi surface and magnetovolume effect.<sup>16</sup> Its extension along the above lines offers a promising approach to the high-temperature behavior. To this end we have calculated  $U$  and  $m_i$  for four basic types of magnetic excitation: (a) spin spirals, (b) alternating tilts, (c) a single reversed spin, and (d) an interacting pair at various angles.

A spin spiral (SS) typifies the slow spatial variation of spin direction  $\hat{m}(\vec{r})$  envisaged by Korenman, Murray, and Prange.<sup>1</sup> They retain only terms involving  $\text{grad}\hat{m}$  and to that accuracy a regular SS suffices to represent the more general spin variation. Our spins were rotated in the  $yz$  plane by an angle  $\alpha$  between successive atomic planes spaced  $\frac{1}{2}a$  (in the bcc structure) along  $[100]$ . The degree of disorder at  $T_C < T < 1.47T_C$  indicated<sup>2, 3</sup> by the spin-wave data<sup>10</sup> corresponds to  $\alpha_0 \approx 36^\circ$ .

We note firstly from the results in Fig. 1 that at  $\alpha_0$  on the SS the calculated self-consistent atomic moment  $m$  has dropped by only 6% from its  $\alpha = 0$  ground-state value. This  $\delta m$  agrees with the experimental indication<sup>12</sup> of "negligible" change. Our  $\delta m$  is comparable to Hubbard's<sup>6</sup> but

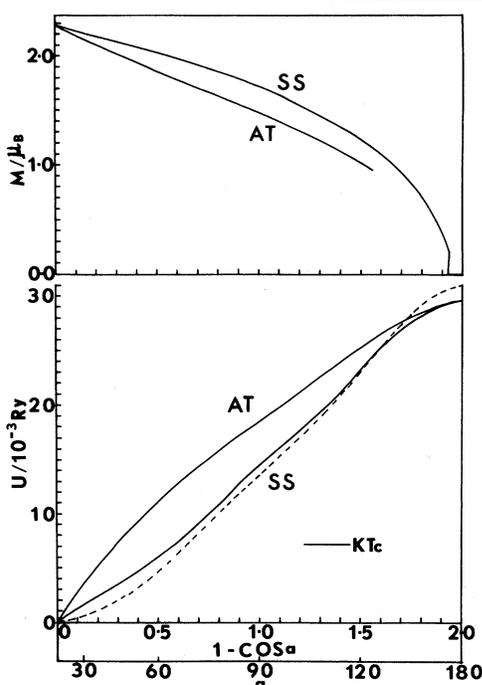


FIG. 1. Atomic magnetic moment  $m$  (in Bohr magnetons  $\mu_B$ ) and energy  $U$  per atom relative to the ferromagnetic ground state, for a spin spiral (SS) and alternating tilt (AT). Results for the SS are shown calculated with  $d$  plus  $s$  bands (full line) and for a  $d$  band only (broken line): For the AT they are practically indistinguishable. The  $\alpha$  is the angle between nearest-neighbor spins. The value of  $kT_C$  is shown for comparison.

substantially less than Hasegawa's<sup>7</sup> 24% drop. For large  $\alpha$  the  $m$  drops rapidly (Fig. 1) becoming zero if one tries to calculate an antiferromagnetic array ( $\alpha = 180^\circ$ ).

Secondly, we note (Fig. 1) that the SS energy  $U_{SS}(\alpha)$  (i) increases slowly with  $\alpha$  for small  $\alpha < 40^\circ$  and (ii) then rises more rapidly for larger  $\alpha$ . We believe that property (i) is responsible for the low  $T_C$  which is the loss of long-range order, while (ii) gives the high degree of short-range order at  $T \geq T_C$ : It costs a lot of energy for neighboring spins to make an angle much greater than  $40^\circ$  with one another. In fact we suggest that the steepness of the slope of  $U_{SS}(\alpha)$  beyond  $40^\circ$  is responsible for the small changes in disorder seen in the spin waves<sup>2</sup> between  $T_C$  and  $1.4T_C$ . From Fig. 1 and other calculations it seems that the rise of  $U_{SS}(\alpha)$  is connected with the reduction in  $m$  at large  $\alpha$ , and so the same mechanism and conclusion about short-range order may well be applicable also to Ni for which spin waves are also observed<sup>11</sup> above  $T_C$ . Our

picture contrasts with a nearest-neighbor Heisenberg model known not to support *well-defined* spin waves above  $T_C$ .<sup>17</sup> We believe that our *ab initio* calculations justify some of the assumptions of Korenman, Murray, and Prange.<sup>18</sup>

For small  $\alpha$ , the  $U_{SS}(\alpha)$  is proportional<sup>19</sup> to the spin-wave stiffness constant  $D$ . We find  $D = 237 \text{ meV \AA}^2$  (calculated with the  $s$  band) compared with the observed  $D = 305 \text{ meV \AA}^2$  extrapolated to  $0^\circ\text{K}$ . Lack of numerical convergence at  $\alpha < 3^\circ$  has been cut off in all our calculations. The  $U_{SS}$  has also been calculated for a  $[110]$  spiral and is very nearly identical to  $U_{SS}([100])$  (Fig. 1) when plotted against spiral angle per unit length.

Our second type of magnetic excitation is the alternating tilt (AT) of spins in which alternate (100) planes of atoms are tilted  $\pm \frac{1}{2}\alpha$  with respect to the  $z$  axis. It is similar to a short-range random fluctuation of spin direction from atom to atom. The energy  $U_{AT}(\alpha)$  (Fig. 1) is much higher than  $U_{SS}(\alpha)$  for the same angle  $\alpha$  between nearest neighbors, which underlines again that the system prefers a slow and *smooth* spatial variation of  $\hat{m}(\vec{r})$  leading to a high degree of short-range order above  $T_C$ .

We have repeated the calculation with the AT superposed on a SS of  $\alpha = 70^\circ$  to represent a paramagnon in the short-range order above  $T_C$ . We find that  $\hbar\omega(q) = 2U_{AT}(\alpha)/S\alpha^2$  decreases from 1230 to 540 meV. This decrease is much larger than expected from the consideration of Ref. 3, and could be interpreted as  $\sim 50\%$  reduction in  $D$ . It suggests short-range order with  $\alpha$  substantially less than  $70^\circ$ .

The small- $\alpha$  limit of  $U_{SS}$ ,  $U_{AT}$ , and other spin fluctuations can be expressed rigorously<sup>20</sup> by a Heisenberg form  $U = -\frac{1}{2}\sum J_{ij}\cos\theta_{ij}$ . If this were true also for large  $\theta_{ij}$  the  $U_{AT}(\alpha)$  would be proportional to  $1 - \cos\alpha$  for all  $\alpha$ , which is manifestly not so (Fig. 1) (contrary to Hubbard<sup>5,6</sup>). The following form to replace  $-J_{ij}\cos\theta_{ij}$  fits all the  $U_{SS}(\alpha)$  and  $U_{AT}(\alpha)$  results for the pure  $d$  band:

$$U = -J_r[(1-4b)\cos\theta_{ij} + b\cos 2\theta_{ij}] \quad (1)$$

$$\approx (\text{const}) - J_r \cos\theta_{ij} \text{ for small } \theta_i. \quad (2)$$

Here  $J_r$  refers to the  $r$ th shell of neighbors,  $b = 0.09$  for all  $r$ ,  $J_1 = 48.5 \text{ meV}$ ,  $J_2 = 68.5 \text{ meV}$ ,  $J_3 = -26.3 \text{ meV}$ ,  $J_4 = -2.3 \text{ meV}$ ,  $J_r \approx 1 \text{ meV}$  for  $r > 4$ . The results with  $s$  band are less complete for fitting but differ only for the SS at small  $\alpha$  and would only give moderate changes in the  $J_r$ . Our  $J_r$  give  $T_C = 1660^\circ\text{K}$  in mean-field theory (classi-

cal statistics), which would be substantially lowered by short-range order effects and raised somewhat by quantum corrections.<sup>4,6</sup>

We have also calculated the  $J_r$  directly as follows. We start with the ferromagnetic ground state, and turn a pair of spins ( $r$ th neighbors) through  $90^\circ$  into the equatorial plane and to an angle  $\alpha$  with one another. The calculations so far relate only to small  $\alpha$ . We obtain  $J_1 = 142$  meV,  $J_2 = 15$  meV,  $J_3 = -10$  meV,  $J_4 = -10$  meV, and  $J_5 = -35$  meV for a pure  $d$  band. The fifth neighbor lies two steps in the [111] direction which may account for the large  $J_5$ . These values of  $J_r$  differ substantially from those above, but note that no set of  $J_r$  can represent all spin configurations. The first set are derived from configurations in which  $m$  varies from its saturation value to zero. In the second set the  $v_i$  are parameters in the sense of the functional integral theory<sup>5,6</sup> and do not satisfy  $2v_i = Im_i$  exactly.

The important point is that both sets of  $J_r$  agree in indicating a short-range ferromagnetic interaction and a comparably strong, longer-range antiferromagnetic one. This is in agreement with the general arguments of Ref. 4 (particularly the last paragraph of Sec. IV and the next to last of Sec. VI), which conversely lead more or less automatically to curves shaped qualitatively as in Fig. 1. Thus our considerations may also apply qualitatively to Ni which also shows well-defined spin waves above  $T_C$ . Certainly the combination of ferromagnetic and antiferromagnetic couplings is known to favor spiraling arrangements, which is how we picture the short-range order.

The combination of ferromagnetic and antiferromagnetic couplings may also explain the strong short-range order above  $T_C$ . A nearest-neighbor Heisenberg model does not show well-defined spin waves above  $T_C$ .<sup>17</sup> A longer-range purely ferromagnetic interaction would approximate more nearly to mean-field theory and presumably show even less short-range order. However, with the mixed couplings,  $T_C$  is determined by the sum of the couplings and is low because of cancellation, whereas the short-range order may be determined more by the relatively stronger near-neighbor ferromagnetic interaction. This suggestion is due to Edwards.<sup>21</sup> We have no resolution of the contradiction between the large short-range order indicated by the spin-wave linewidths<sup>1-4,10</sup> and the magnetic entropy deduced from the specific heat<sup>22</sup>: We suggest that fluctuations in  $|\vec{m}|$  may be significant, and the possibil-

ity of atom-to-atom fluctuations superposed onto more slowly varying short-range order.

Our results for a single reversed spin are similar to those of Hubbard<sup>5,6</sup> with quantitative differences.

In conclusion, our calculations are consistent with short-range order in Fe above  $T_C$  envisaged as a spiraling sort of arrangement of spins. Further details of the work will be published elsewhere in due course.<sup>23</sup>

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