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Magnetism of nickel

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A previously developed theory of the magnetism of iron, based upon notion of a randomized exchange field, has now been applied to calculate the properties of nickel. We obtained a Curie temperature of 1200 K, about twice the observed value. The magnetization curve, the paramagnetic susceptibility (a Curie-Weiss law), and the distribution of spin lengths are also calculated. Both similarities and differences from the results of the iron calculations are noted.

I. INTRODUCTION

In two previous papers[1,2] we discussed the calculation of the magnetic properties of iron on the basis of a randomized exchange field model using the formalism developed by Schrieffer *et al.*[3] and Cyrot.[4] In particular it was shown that this model could at the same time give reasonable values for both the saturation moment and the Curie temperature, which had not been possible with the more usual itinerant or Heisenberg models. Indeed this model provides a kind of synthesis of the latter models. Other properties of iron were also calculated and found to be in moderately good agreement with experiment. The question then naturally arises as to whether similar results would be obtained by the application of the method to nickel.

Whereas iron might be thought the best candidate among the transition metals for the application of the localized model, it has long been supected that nickel might be markedly more itinerant in its character, although the good Curie-Weiss law observed for the paramagnetic susceptibility in nickel calls this into question. The randomized exchange field model allows one to investigate this question. It makes no assumption that requires the atomic-spin length to be constant (and merely rotated from its ground-state value), but allows the possibility of variability of both the spin length and direction, as would be required by very itinerant behavior. In fact, in the iron calculations we found that the atomic-spin magnitude remained almost constant over a wide range of temperature in spite of this freedom in the theory. In the nickel calculation we found something different. The atomic-spin magnitude did change with temperature, decreasing as one approaches the Curie temperature, mimicing in some degree the temperature behavior of the exchange splitting observed by Eastman *et al.*[5] However, while the mean spin magnitude changes, the variance of the atomic-spin magnitudes about their mean is not particularly greater than that calculated for iron, a result not especially in keeping with a very itinerant model for nickel. We also obtained a paramagnetic susceptibility which fitted very well to a Curie-Weiss law, a feature characteristic of a localized model. On the whole the results we obtain for nickel are very similar to those for iron apart from one or two striking differences such as that just mentioned.

In Sec. II we will give one or two details of the method of calculation (basically the same as that used in the iron calculations[2]). In Sec. III we discuss the results in a little more detail and draw some tentative conclusions.

II. METHOD OF CALCULATIONS

The method of calculation was exactly the same as that used in the iron calculations[2] (with the Coulomb-field corrections described there), but with different parameters. The band structure used was derived from that calculated by Callaway and Wang[6] using a Kohn-Sham-Gaspar exchange potential.[7] We combined their up and down spin densities of states to obtain an average density of states and then chose the Fermi energy and exchange splitting to give the correct number of d electrons (9.4) and ground-state moment (0.6); the exchange splitting required was 0.79 eV (compared to 2 eV in Fe). These figures correspond to an exchange interaction parameter $K = 1.32$ eV (in the notation of Ref. 2) compared to $K = 0.9$ eV for iron.

Convergence of the self-consistent equations [Eq. (22) of Ref. 2] was considerably more difficult than in the iron case, particularly for temperatures near T_C. This may be because antibound states (generated in the majority spin band by the random exchange potential) cross the threshold into the band at these temperatures.

III. RESULTS AND CONCLUSIONS

As in the case of iron,[2] our basic calculation was of the function $E(\vec{v})$ which gives the average energy of an atom with an exchange field $\vec{v}$ and depends upon the temperature T. In Fig. 1 we compare the ground state ($T=0$) $E(\vec{v})$ of iron and nickel for $\vec{v}$ of the form $\vec{v}=(0,0,v_z)$ (the z direction is that of the magnetization). They are markedly different in shape as well as magnitude. The Ni curve shows no shoulder of the kind found for iron; indeed, it rises more sharply in the corresponding region, and closely resembles a parabola slightly compressed on the right. In the case of iron[2] we found that $E(\vec{v})$ could be well fitted by a formula of the kind

$$E(\vec{v}) = E_0(v) + A v_z \ , \qquad (1)$$

where $v=|\vec{v}|$. No such simple fit for $E(\vec{v})$ could be obtained in the nickel case for $T < T_C$.

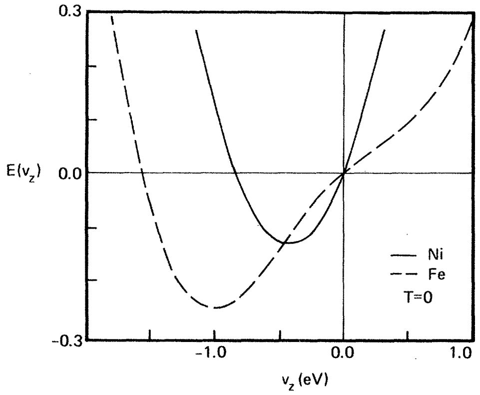

FIG. 1. Ground state $E(\vec{v})$ for iron and nickel plotted as a function of $\vec{v}_z$ for v of the form $\vec{v}=(0,0,v_z)$.

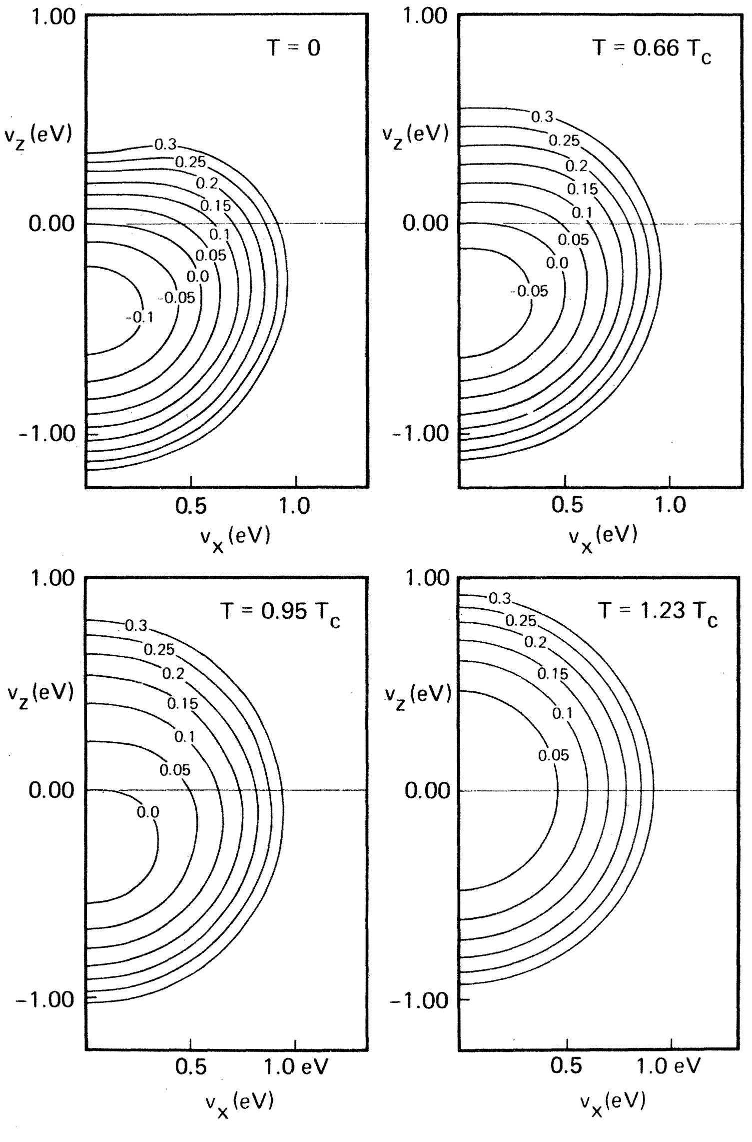

FIG. 2. $E(\vec{v})$ contours for nickel at several temperatures; the contours are labeled in eV.

In Fig. 2 we show the contours of $E(\vec{v})$ in the $v_x v_z$ plane at several temperatures [the $E(\vec{v})$ are symmetric under rotations about the magnetization direction]. Above $T = 1200$ K the contours become symmetric about the origin, so we take this to be the Curie temperature, $T_C = 1200$ K. This is about 88% higher than the observed Curie temperature (the corresponding figure for iron was 75%). As in the iron case, all refinements of the theory are expected to reduce this estimate. It may be noted that, although the ratios of the Curie temperatures, the exchange splittings and ground-state moments of iron and nickel are all different, the model has given a good value for the Curie-temperature ratio. At the higher temperatures the $E(\vec{v})$ contours look very different from those for iron; in particular they do not show an annular valley for $T > T_C$ found in the iron case; $E(\vec{v})$ simply increases monotonically with increasing v. This is exemplified in Fig. 3 where we compare the $E(\text{v})$ for iron and nickel in the paramagnetic region [above T_C $E(\vec{v})$ is a function of v only]; the $E(\text{v})$ for nickel has no minimum.

In Fig. 4 we compared the magnetization curve calculated for nickel with the similar calculation for iron and the experimental curve for nickel. While the calculated curve is in poor agreement with experiment, it is distinctly better than the fit for iron. On the other hand, the experimental curves for iron and nickel are closely similar. It is clear that the present model throws no light on this point.

The paramagnetic susceptibility was calculated using the methods described in Ref. 2. As in the iron case we obtained a very good fit to the Curie-Weiss law

$$\chi = \frac{1}{3}\frac{m_{\text{eff}}^2}{T - T_C}\,, \qquad (2)$$

for nickel we find $m_{\text{eff}} = 0.49\mu_B$. This m_{eff} is substantially less than the ground-state moment, quite different from the iron case where we obtained a m_{eff} greater than the ground-state moment. However it agrees well with our calculated value for the atomic-spin length in the paramagnetic region (see below), which was not the case for the corresponding iron calculation.

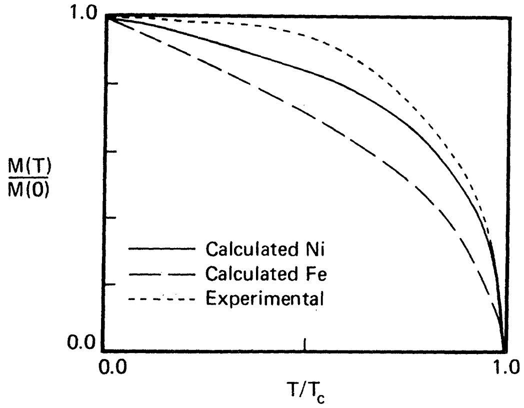

FIG. 4. Calculated magnetization curves for nickel and iron compared with the experimental curve for nickel.

We also calculated the root-mean-square average $(\langle S^2 \rangle)^{1/2}$ of the atomic-spin length. In the iron case this quantity hardly changed from its ground-state value over the whole temperature range studied. However, in nickel we found that this average decrease by about 25% as T increased from $T = 0$ to T_C, but was nearly constant (increasing very slightly) in the paramagnetic region (see Fig. 5). This behavior mimics that of the exchange splitting observed by Eastman *et al.*[5] in nickel, although he saw a 40% drop in the splitting, and exact connection between his observations and the atomic-spin length is not clear.

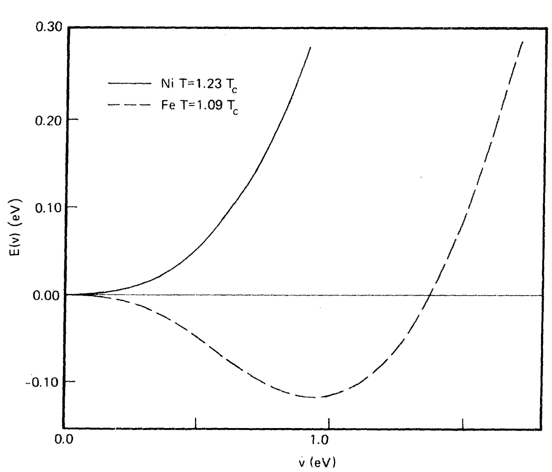

FIG. 3. $E(\vec{v})$ vs $\text{v} = |\vec{v}|$ for nickel and iron in the paramagnetic region.

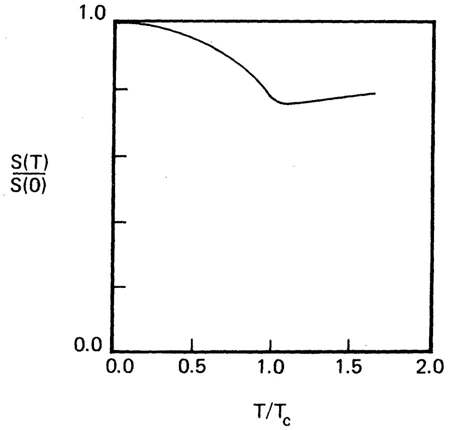

FIG. 5. Root-mean-square atomic-spin magnitude calculated for nickel as a function of the temperature T.

The change in the atomic-spin length with temperature is inconsistent with a localized Heisenberg model, but easily accommodated in an itinerant theory. In the latter type of theory one would expect a large variability of the spin length which might well lead to a reduction of the mean spin with temperature. Indeed, in Stoner theory the atomic spin disappears altogether above the Curie temperature. It is therefore of interest to investigate the distribution of atomic-spin lengths as we did in the iron case, especially in the paramagnetic region. In Fig. 6 we compare the calculated atomic-spin distributions for iron and nickel in the paramagnetic region. We see, in fact, that the two curves have very much the same shape. It is simply that the peak of the nickel curve has moved away from the ground-state value whereas that of iron remained on the ground-state value. Otherwise there is little difference; in particular the nickel curve shows no evidence that the spin length is randomly distributed between 0 and some finite upper limit.

What conclusions might one draw from these results? First we note that, as in the iron case, we have been successful in obtaining at the same time the correct value for the ground-state moment and a Curie temperature of the right order of magnitude, a feat which has proved impossible in the ordinary itinerant theory. The ratio of the calculated Curie temperatures for the two metals is about the same as that observed, suggesting that the discrepancy between the calculated and observed Curie temperatures may be of the same origin in both cases [perhaps a consequence of the use of approximations (see Ref. 2) which are equivalent to mean-field theory from the point of view of a localized model]. On the whole the results for nickel are very similar to those for iron. Basically we seem in both cases to be dealing with something like a localized spin model but with some itinerant aspects grafted on. The latter aspects are a little more pronounced in the nickel case, e.g., in the variation of atomic-spin length with temperature.

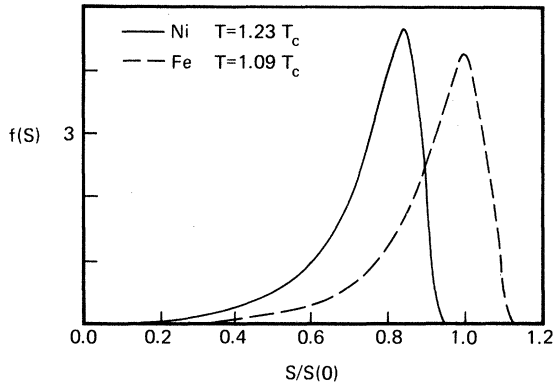

FIG. 6. Distribution functions $f(S)$ for the atomic-spin lenghts calculated for iron and nickel in the paramagnetic region; $S(0)$ is the ground-state atomic spin.

Clearly some improvements are needed in the general theory. In particular one needs to account for the factor of 2 difference between the calculated and observed Curie temperatures and for the failure of the theory to give good magnetization curves. In connection with the latter it may be remarked that part of the trouble lies with the fact that the theory as formulated in Refs. 1 and 2 treats the atomic spins as classical rather than quantum mechanical. The effect of this can be clearly seen in Fig. 4, which shows the calculated ratios $M(T)/M(0)$ emerging from $T=0$ with a finite slope rather than the zero slope required by spin-wave theory.

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[*] Deceased. *Note added in proof:* Additional results on nickel, calculated by a different method, are to be found in Hubbard's contribution to the *Taniguchi International Symposium on Electron Correlation and Magnetism in Narrow Band Systems, Susono, Japan, November 1–6 1980* (Springer, Berlin, in press).

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