[2]D. G. Carlson, A. Segmüller, E. Mosekilde, H. Cole, and J. A. Armstrong, Appl. Phys. Lett. 18, 330 (1971).
[3]D. L. White, J. Appl. Phys. 33, 2547 (1962).
[4]D. G. Carlson and A. Segmüller, Phys. Rev. Lett. 27, 195 (1971).
[5]A double-peaked form for the *linear* gain due to impurity bands has been found under certain conditions by E. Mosekilde, unpublished. We thank Dr. Mosekilde for the preprint prior to publication.
[6]N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965), Chap. 2.
[7]C.-C. Wu and H. N. Spector, unpublished. This paper treats acoustic second-harmonic generation in a nondegenerate electron gas. We wish to thank the authors for sending us a preprint prior to publication.
[8]E. J. Woll, Jr., and W. Kohn, Phys. Rev. 126, 1693 (1962).
[9]S. S. Jha, Phys. Rev. 150, 413 (1966).

Temperature Dependence of the Hyperfine Field at Iron Atoms near 3*d* Impurities

I. Vincze and G. Grüner
Central Research Institute for Physics, Budapest, Hungary
(Received 27 September 1971)

The temperature dependence of the hyperfine field at Fe atoms was determined by Mössbauer and continuous-wave NMR methods for Fe-based alloys containing Ti, V, Cr, Mn, Co, and Ni impurities. A marked anomaly was found in the case of Mn, and a lesser one for Ni. The temperature anomaly of the hyperfine field at iron atoms in the neighborhood of Mn impurities can be described with a linear combination of two terms, one proportional to μ_{Fe}, the other to $\mu_{Mn}-\mu_{Fe}$. We suggest that the latter is brought about by the conduction-electron polarization.

The temperature dependence of the moment of a magnetic impurity in a metallic ferromagnet may be different from that of the matrix. The first observation of such behavior was of the anomalous temperature dependence of the Mn hyperfine field in iron.[1] According to Jaccarino, Walker, and Wertheim[2] the explanation of this fact given by the molecular field approximation of the Heisenberg model is that impurity-host exchange is smaller than the host-host exchange interaction, so that consequently the impurity moment decreases more rapidly with temperature than that of the matrix.

On the other hand, according to the Heisenberg model itself, the magnetization of iron atoms around an impurity is different from that of the matrix because of the different exchange fields acting on them. This leads to an anomalous behavior of the hyperfine fields at iron atoms near the impurity through the core-polarization contribution H_{CP} of the hyperfine field. Cranshaw, Johnson, and Ridout[3] interpreted the temperature dependences they found at the first neighbors of the Mn impurities in a Fe–7.5 at.% Mn alloy between 80 and 500°K in this way, but found no good agreement between theory and experiment.

The aim of this paper is to report on the investigation of the temperature dependence of the hyperfine-field distribution around 3*d* impurities in iron. By performing measurements of this nature one can hope to get some information about the mechanism of the anomalous temperature dependences found with various ferromagnetic alloys.

The Mössbauer effect (ME) measurements were performed on iron alloys with the following impurities: Ti (3.0 at.%), V (2.0 and 5.0 at.%), Cr (2.2 at.%), Mn (2.5 and 3.4 at.%), Co (3.0 at.%), and Ni (3.0 and 5.0 at.%). The cw NMR experiments were performed on alloys with V (0.5 at.%), Cr (2.2 at.%), Mn (1.0 at.%), and Co (0.7 at.%). For the ME and cw NMR experiments, conventional equipment[4,5] was used, with temperatures between 77°K and the Curie point T_c for the former, and between 77°K and room temperature for the latter.

To limit the number of parameters, the Mössbauer spectra were decomposed assuming random distribution of impurities and an additive effect caused by the impurities. We believe these assumptions are not too wrong because of the low impurity concentration. A detailed χ^2 test was performed for each spectrum taken at room temperature to obtain the least number of parameters that gives a good fit for the spectra. The hyperfine-field shifts at the first (ΔH_1) and second (ΔH_2) iron neighbors of the impurities at room temperature follow. For Ti,

$$\Delta H_1 = \Delta H_2 = -19.1 \pm 0.3 \text{ kG};$$

for V,

$$\Delta H_1 = \Delta H_2 = -24.4 \pm 0.4 \text{ kG};$$

and for Cr,

$$\Delta H_1 = \Delta H_2 = -26.9 \pm 0.2 \text{ kG}.$$

(In these cases the shifts at the first and second neighbors could not be resolved separately, because their magnitudes are nearly the same.) For Mn,

$$\Delta H_1 = -23.0 \pm 0.1 \text{ kG}, \quad |\Delta H_2| < 3 \text{ kG};$$

for Co,

$$\Delta H_1 = 13.3 \pm 0.5 \text{ kG}, \quad \Delta H_2 = 6.0 \pm 1.0 \text{ kG};$$

and for Ni,

$$\Delta H_1 = 9.4 \pm 0.3 \text{ kG}, \quad \Delta H_2 = 7.0 \pm 1.0 \text{ kG}.$$

All the above data are in good agreement with previous results of spin-echo,[6,7] cw NMR,[8] and Mössbauer[9] measurements.

Figure 1 shows the temperature dependence of the difference of the relative hyperfine field of Fe atoms, without and with nearest-neighbor impurities, normalized to the value taken at 80°K. There is a large anomaly in the case of Mn and a smaller one in the case of Ni impurities, while for other impurities no deviation was found within the experimental error. The temperature dependence of the hyperfine field at iron atoms without first-neighbor impurities is the same as that of pure iron.

The anomaly found in the case of Ni is in agreement with that observed between 77 and 350°K at the third-neighbor iron sites.[10] We could not follow by ME the temperature dependences of the second-neighbor shifts in the case of the Mn, Ni, and Co impurities because of their small value.

The hyperfine-field shifts at the more distant neighbors were detected by the cw NMR method. The room-temperature spectra were similar to those measured by Mendis and Anderson.[8] Figure 2 shows the temperature dependence of the central resonance and satellite for Mn and Co impurities. For these, as well as for V and Cr impurities, the temperature dependence of the satellites is the same as that of the central resonance within experimental error (0.05%).

The hyperfine field at an iron nucleus has two components: the core-polarization contribution H_{CP}, which is proportional to the magnetic moment of the atom itself, and the conduction-electron–polarization component H_{CEP}, which reflects the influence of the neighboring atoms. The anomaly can, in principle, be brought about by an anomalous temperature dependence of both terms.

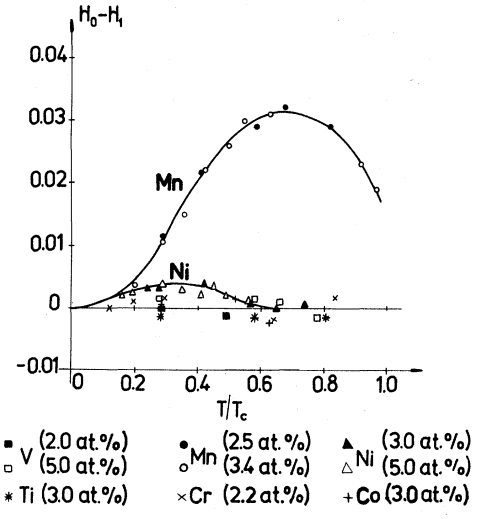

FIG. 1. The difference of the relative hyperfine field of iron atoms without (H_0) and with (H_1) impurity nearest neighbors.

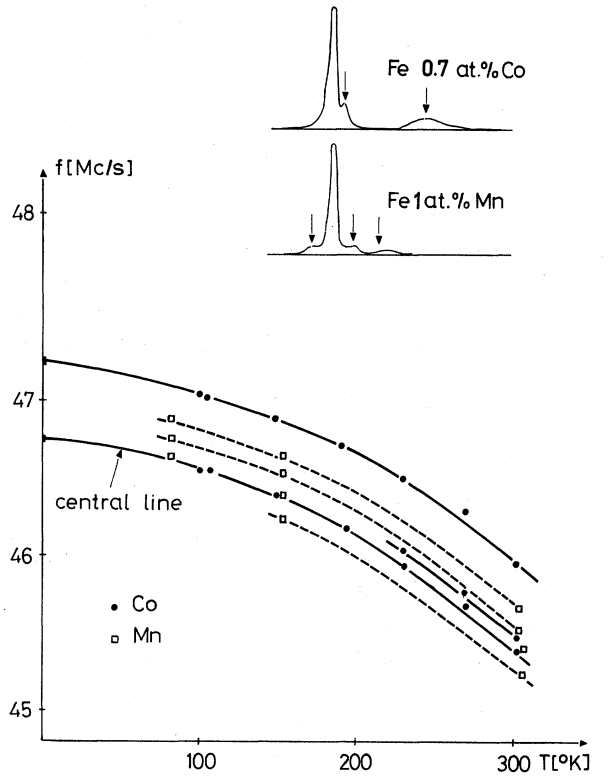

FIG. 2. Temperature dependence of the hyperfine-field shifts at iron atoms in the case of Co and Mn impurities detected by the cw NMR method. The spin-echo data of *Fe*Co alloys (Ref. 7) taken at 1.3°K are included in the figure too.

At first sight it might seem possible to describe the anomalies found in the case of Mn and Ni impurities in terms of the Heisenberg model, in which these are attributed to the anomalous behavior of the iron moment around the impurities, due to the different exchange fields, that is reflected in the component H_{CP} of the hyperfine field. However, according to this model a similar anomaly is expected with all the impurities, because exchange between the impurity and the matrix is different from exchange between the matrix atoms. Thus, the absence of the anomaly with Ti, V, Cr, and Co and nonmagnetic impurities like Al, Ga, and Sn[4] indicates that the anomalous temperature dependence of the hyperfine field found at the first neighbors of Mn and Ni impurities has some other origin. This conclusion is supported by the fact that the temperature dependence of the core-polarization contribution calculated in terms of the Heisenberg model[3] is different from the measured $\Delta H_1(T)$. On the other hand, we can give an upper limit for the change of the core-polarization contribution between 80 and 300°K on the basis of average magnetization measurements. The relative magnetization of a Fe–3.9 at.% Mn alloy[11] (σ_{alloy}) differs from that of pure iron (σ_{Fe}) only by $\Delta\sigma = \sigma_{Fe} - \sigma_{alloy} = 0.006 \pm 0.002$ at room temperature, which is a result partly of the lower Curie temperature of the alloy (contributing more than 0.002 to $\Delta\sigma$) and of the faster decrease of the Mn moment (contributing more than 0.004 to $\Delta\sigma$). Thus the anomalous decrease of the iron moments around Mn impurities, if it exists, cannot be more than $0.01\mu_B$, and so the core-polarization contribution to the anomalous change of $\Delta H_1 = 3.6$ kG observed between 80 and 300°K is less than 0.6 kG [the core-polarization coupling constant, $(60\text{ kG})/\mu_B$,[12] was used].

We suggest therefore, that the anomalous first-neighbor hyperfine-field behavior is the consequence of the anomalous behavior of the impurity moment. First of all, a marked anomaly in the temperature dependence of ΔH_1 was observed for Mn impurity whose magnetic moment is known to show a very anomalous temperature dependence. This anomalous temperature dependence is reflected at the site of the first neighbors, so we can try to fit our data obtained for a Mn impurity by a linear combination of two components proportional to μ_{Fe} and $\mu_{Fe} - \mu_{Mn}$:

$$\Delta H_1(T) = A\mu_{Fe}(T) + B[\mu_{Fe}(T) - \mu_{Mn}(T)], \qquad (1)$$

where $\mu_{Fe}(T)$ and $\mu_{Mn}(T)$ are the Fe and Mn moments. As the temperature dependence of μ_{Mn} has not been measured by diffuse neutron scattering, we have only indirect information on $\mu_{Mn}(T)$. The dashed lines in Fig. 3 show the temperature dependences of the contribution proportional to $\mu_{Fe} - \mu_{Mn}$ given by making two different assumptions about the contribution H_{CEP} to the Mn hyperfine field. In calculating curve 1 it was supposed that this contribution is equal to the contribution H_{CEP} of the iron, and thus $H_{Fe} - H_{Mn} \sim \mu_{Fe} - \mu_{Mn}$; while for curve 2 the value $H_{CEP}^{Mn} = 160$ kG,[12] the Mn moment at 80°K, $\mu_{Mn} \simeq 1.1\mu_B$,[13] and the core-polarization coupling constant, $(60\text{ kG})/\mu_B$,[12] are used. Different parameters alter only the steepness of the $\mu_{Fe} - \mu_{Mn}$ curve; the characteristic peak at $T/T_c = 0.6$ remains unchanged. The dots show the contribution proportional to the matrix moment. The linear combination of the two curves (curve 1 and μ_{Fe} or curve 2 and μ_{Fe}) describes the temperature dependence of ΔH_1 rather well (solid line). Of course this description is not unambiguous, as equally good agreement can be obtained with other parameters [$A = -(2.3\text{ kG})/\mu_B$, $B = -(13.6$

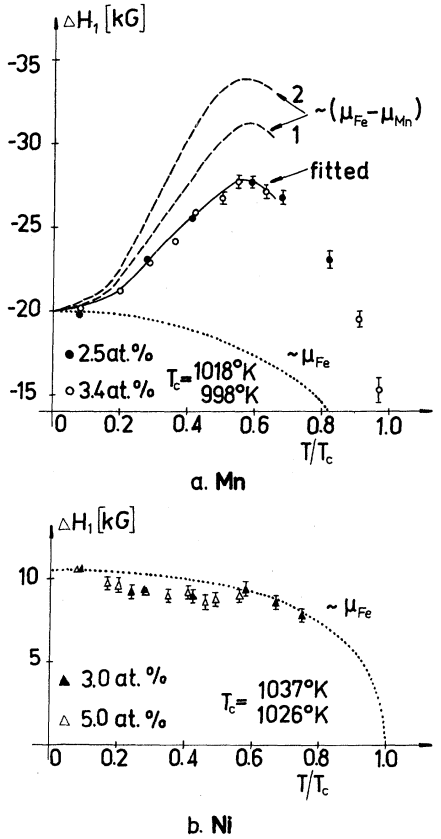

FIG. 3. The change of the hyperfine field due to the impurity at the first-neighbor iron atoms as a function of temperature. The meaning of the curves is explained in the text.

kG)/μ_B for curve 1; and $A = -(3.8\ \text{kG})/\mu_B$, $B = -(10.6\ \text{kG})/\mu_B$ for curve 2]. However, the curvature of the measured ΔH_1, and especially the strong peak around $T/T_c = 0.6$, supports the idea that the anomaly is caused by the contribution proportional to $\mu_{Fe} - \mu_{Mn}$.

The success of fitting our data by Eq. (1) suggests that the anomaly is brought about by the anomalous temperature dependence of the impurity moment. This anomalous behavior, in our opinion, is reflected at the site of the first neighbors through the conduction-electron–polarization contribution to the hyperfine field. The change of the CEP contribution due to the impurity is proportional to $\mu_{Fe} - \mu_i$ because it reflects the change in the Ruderman-Kittel-Kasuya-Yosida spin-density oscillation. We can estimate whether this mechanism is effective enough to explain the magnitude of the anomaly. The change of the hyperfine field at the first iron neighbors around a nonmagnetic Al impurity[4,9] (which is a "magnetic hole") is -22 kG, so $B = -(10\ \text{kG})/\mu_B$, which is in good agreement with the B value obtained from the fit with Eq. (1).

For Ni impurities the detailed temperature dependence of the Ni hyperfine field is not known, so it is not possible to make such a detailed comparison as in the case of Mn. However, the anomaly seems to be well describable in the same way as in the Mn case if it is assumed that μ_{Ni} decreases a little more rapidly than μ_{Fe} (at room temperature the relative hyperfine field at Ni atoms[14] is smaller than that of the iron), and hence causes a rise in the absolute value of the negative contribution proportional to $\mu_{Fe} - \mu_{Ni}$.

Preliminary measurements show an anomalous temperature dependence of the first-neighbor iron hyperfine field similar to that of Mn in the case of Ru and Os, and a dependence similar to that of Ni in the case Pd and Pt.

These data seem to confirm Campbell's suggestion[15] that the anomalous temperature dependence of the impurity moment is the consequence of an electron-band perturbation due to charge screening of the impurity near the Fermi level.

We wish to thank Professor L. Pál for his continuous interest in this work, and Dr. C. Hargitai and Dr. A. Zawadowski for helpful discussions. We are indebted to Dr. G. Konczos for preparing the samples.

[1]Y. Koi, A. Tsujimura, and T. Hihara, J. Phys. Soc. Jap. 19, 1493 (1964).
[2]V. Jaccarino, L. R. Walker, and G. K. Wertheim, Phys. Rev. Lett. 13, 752 (1964).
[3]T. E. Cranshaw, C. E. Johnson, and M. S. Ridout, Phys. Lett. 20, 97 (1967).
[4]I. Vincze and L. Cser, to be published.
[5]F. I. Tóth, K. Tompa, and G. Grüner, to be published.
[6]R. H. Dean, R. J. Furley, and R. G. Scurlock, J. Phys. F: Metal Phys. 1, 78 (1971).
[7]J. I. Budnick, T. J. Burch, S. Skalski, and K. Raj, Phys. Rev. Lett. 24, 511 (1970).
[8]E. F. Mendis and L. W. Anderson, Phys. Status Solidi 41, 375 (1971).
[9]G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. Lett. 12, 24 (1964).
[10]P. C. Riedi, Phys. Lett. 33A, 273 (1970).
[11]C. Sadron, Ann. Phys. (Paris) 17, 371 (1932).
[12]I. A. Campbell, J. Phys. C: Proc. Phys. Soc., London 2, 1338 (1969).
[13]D. A. Shirley, S. S. Rosenblum, and E. Matthias, Phys. Rev. 170, 363 (1968).
[14]R. L. Streever, L. H. Bennett, R. C. La Force, and G. T. Day, J. Appl. Phys. 34, 1050 (1963).
[15]I. A. Campbell, J. Phys. C: Proc. Phys. Soc., London 3, 2151 (1970).