resolved fluorine superhyperfine structure, but the resolution of this structure was noticeably poorer than that observed for the other fluorite crystals. In an attempt to observe the superhyperfine structure with improved resolution, we investigated a series of BaF_2 crystals with lower Mn^{2+} concentrations. However, the ESR spectra from these crystals did not display any better resolution. This fact is reflected in Table I by the relatively large error limits for the BaF_2 system.

We have also found that the linewidths of the best-fitted theoretical spectra for BaF_2 varied with crystal orientation, i.e., the linewidths for the [100], [110], and [111] spectra were found to be 7, 5, and 6 G, respectively. As shown in Table I, the other systems all have a best-fitted linewidth of 2.1 G, independent of the crystal orientation.

This behavior of the BaF_2 data can be explained if it is assumed that the Mn^{2+} ions tend to cluster in the BaF_2 lattice, which has a larger lattice parameter than the other fluorite lattices. The major contribution to the observed linewidth would then be due to the dipole-dipole interaction between Mn^{2+} ions in this cluster. As a test of this hypothesis, we calculated the second moment for the Mn^{2+} ESR line assuming all the nearby Ba^{2+} sites were occupied by Mn^{2+} ions up to the tenth shell. The resultant second moment displayed an angular variation which is consistent with the trend exhibited by the measured best-fitted linewidth for the three crystallographic directions.

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Differences in the Temperature Dependence of the Hyperfine Field and Magnetization of Ferromagnetic Metals

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The temperature dependences of the magnetization and of the hyperfine field in ferromagnetic metals such as Fe or Ni are different even after transformation to constant volume. It is suggested that the effect of lattice vibrations can explain the observed explicit temperature dependence of the hyperfine field at constant volume and that the deviation of the latter from the temperature dependence of the magnetization at constant pressure is well described by considering the thermal expansion also. Some applications of this model to related problems are discussed.

In a pure ferromagnetic metal at constant pressure, the temperature dependence of the hyperfine field is not precisely the same as that of the spontaneous magnetization. The first observation of this effect was the nuclear-magnetic-resonance (NMR) measurement of Robert and Winter[1] in iron. The agreement between the temperature dependence of the hyperfine field measured by NMR and the Mössbauer effect (ME) indicates[2] that the deviation of the hyperfine field and bulk magnetization with increasing temperature is not connected with the domain structure of the metal, because the NMR measurements are associated with nuclei within the domain walls, while the ME measurements involve chiefly nuclei within the domains themselves.

When the temperature dependence of the reduced hyperfine field h is compared with the reduced magnetization σ, transforming both to constant volume to eliminate any differential effects of thermal expansion, it is found[2,3] that even at constant volume there still remains an explicit temperature dependence of the hyperfine coupling constant A, i.e.,

$$h(T)=A(T)\sigma(T). \qquad (1)$$

The explicit temperature dependence of A for pure iron between 0 and 300 °K can be fitted within experimental accuracy to

$$A(T)=1-aT^2, \qquad (2)$$

where $a=0.77\times10^{-7}\ {}^\circ\mathrm{K}^{-2}$ (Ref. 3) or $0.4\times10^{-7}\ {}^\circ\mathrm{K}^{-2}$ (Ref. 2) is obtained, depending on the magnetization data used.

The situation is similar[4] for Ni, except that at constant pressure the deviation between the temperature dependence of the relative hyperfine field and the relative magnetization is approximately twice as large. After the temperature dependences at constant pressure have been corrected to constant volume there remains an explicit temperature dependence of A, although its functional form is uncertain because of the larger error of the data compared with that for iron. The fit of Eq. (2) to the data gives[5] $a = (0.55 \pm 0.70) \times 10^{-7}$ °K^{-2} or $(0.33 \pm 0.30) \times 10^{-7}$ °K^{-2}, according to the different Ni hyperfine-field measurements.

At present there are no data available for the temperature dependence of the hyperfine field in pure Co.

The possible origins of these differences between the temperature dependence of the hyperfine field and magnetization were discussed in detail by Butler *et al.*[2] They assumed the generally used simplifying decomposition of the hyperfine field to two main components of similar value[6,7]:

$$H_{\mathrm{hf}} = H_{\mathrm{CP}} + H_{\mathrm{CEP}} \tag{3}$$

where H_{CP} is the core-polarization contribution due to polarization of the inner and outer s electrons by the magnetic moment of the atom itself (the latter represents s-d mixing) and H_{CEP} is the conduction-electron-polarization component, which reflects the influence of neighboring atoms. The intrinsic temperature dependence of A was attributed to the core-polarization term via three possible mechanisms: (i) Stoner-like electron excitations coupled with a strongly energy-dependent hyperfine coupling constant, giving a T^2 dependence[3] in A; (ii) changes in the intrinsic s-d hybridization due to the change in magnetization; and (iii) phonon admixture of the s and d wave functions. It was concluded that differentiation between the three mechanisms is not possible on the basis of low-temperature measurements.

In the following it will be shown that the temperature dependence of A at constant pressure up to high temperatures can be described well within a simple semiempirical model which takes into account the effect of lattice vibrations. A similar explanation was given by Benedek and Kushida[8] for the explicit temperature dependence of the Knight shift found in alkali metals at constant volume, but, as will be shown later, it also accounts for the measured explicit temperature dependence of other microscopic quantities. We discuss the constant pressure value of A for the reason that at high temperatures the pressure dependences of the hyperfine field and magnetization are not at present known and thus their transformation to constant volume is not possible.

It will be assumed that the temperature dependence of the H_{CP} contribution is the same as that of the atom's own magnetic moment, i.e., $H_{\mathrm{CP}}(T) = H^0_{\mathrm{CP}}\sigma(T)$, where H^0_{CP} is the value of the core-polarization contribution to the hyperfine field at zero temperature. The H_{CEP} contribution coming from neighboring atoms contains the effect of polarization of the 4s conduction band by the d moments; its asymptotic form is the well-known Ruderman-Kittel-Kasuya-Yoshida (RKKY) conduction-electron spin-density-oscillation contribution and thus it can reasonably be assumed to be distance dependent in addition to being proportional to the moment of the surrounding atoms, that is,

$$H_{\mathrm{CEP}}(T) = \langle H_{\mathrm{CEP}}(r(T,t))\rangle\, \sigma(T).$$

Here the brackets indicate averaging over time, and $r(T,t) = r_0 + \Delta r(T) + x(T,t)$ is the distance between the atoms at a given temperature and moment, where r_0 is the value of the distance between the atoms at zero temperature, $\Delta r(T)$ is its change due to thermal expansion, and $x(T,t)$ is the change of the interatomic distance due to thermal vibration around the mean distance [i.e., $\langle x(T,t)\rangle = 0$].[9] Expanding $H_{\mathrm{CEP}}(r)$ around r_0, we have, for the time-average value of $H_{\mathrm{CEP}}(r)$,

$$\langle H_{\mathrm{CEP}}(r)\rangle = H^0_{\mathrm{CEP}} + H'_{\mathrm{CEP}}(r_0)\Delta r(T) + \tfrac{1}{2}H''_{\mathrm{CEP}}(r_0)\langle x^2\rangle\ , \tag{4}$$

where H^0_{CEP} includes the contribution from zero-point vibrations, the prime signifies the derivative with respect to the argument, and $\langle x^2\rangle$ denotes the temperature-dependent part of the average. Using the above expressions, the relative hyperfine field is obtained as

$$h(T) = \frac{H_{\mathrm{hf}}(T)}{H^0_{\mathrm{hf}}} = \left[1 + \frac{H'_{\mathrm{CEP}}}{H_{\mathrm{hf}}}\left(\frac{H'_{\mathrm{CEP}}(r_0)}{H^0_{\mathrm{CEP}}}\,\Delta r(T) + \frac{1}{2}\,\frac{H''_{\mathrm{CEP}}(r_0)}{H^0_{\mathrm{CEP}}}\,\langle x^2\rangle\right)\right]\sigma(T). \tag{5}$$

The explicit temperature dependence of $A(T)$ in Eq. (1) at constant volume thus gives the term in Eq. (5) proportional to $\langle x^2\rangle$, which well explains its observed T^2 dependence at low temperatures and the apparent linear relationship[2] at higher temperatures. Estimation of the magnitude of the terms proportional to $\Delta r(T)$ and $\langle x^2\rangle$ is not easy, because so far as we know there is no exact theoretical calculation of the distance dependence of $H_{\mathrm{CEP}}(r)$. In the following, it will be demonstrated that the two terms have a very similar temperature dependence.

First of all, for temperatures well above the Debye temperature, both terms are proportional

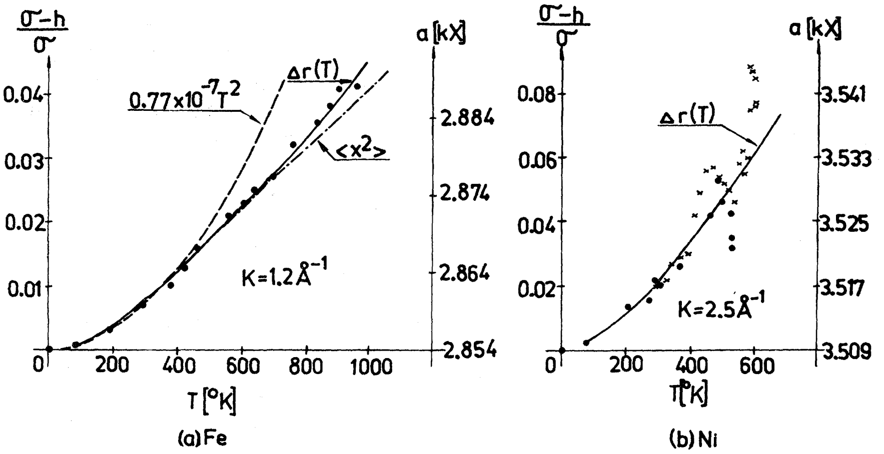

FIG. 1. Temperature dependence of $(\sigma-h)/\sigma$ at constant pressure. [Magnetization data were taken from Ref. 10; the hyperfine-field data for iron are our own Mössbauer data, while those for nickel are from Ref. 4 (full points) and from Ref. 11 (crosses).] The solid lines show the change of the lattice parameter $\Delta r(T)$ due to thermal expansion (Ref. 12). The dashed line represents the approximation of Ref. 3, while the dot-dashed line is the temperature dependence of $\langle x^2\rangle$.

to T, and at low temperatures proportional to T^2. Figure 1(a) shows the temperature dependences of the lattice parameter and of $\langle x^2\rangle$ for iron, where the latter was calculated in the Debye model using the Debye temperature $\Theta_D = 460$ °K taken from specific-heat measurements.[13] The deviation of the two temperature dependences does not exceed 5% in the whole temperature range of interest. Thus from Eq. (5) we can write

$$[\sigma(T) - h(T)]/\sigma(T) = K\Delta r(T) \quad , \qquad (6)$$

where K is a proportionality constant. Figure 1 shows that the agreement for iron and nickel is satisfactory. The figure for iron contains for the hyperfine field the results of our own Mössbauer measurements performed on a spectrographically pure (99.95%) polycrystalline iron foil of 20-μ thickness (Johnson, Matthey Ltd.).[14] The hyperfine-field data agree well with those of Butler *et al.*[2] up to 550 °K (their highest temperature), and lie between the data of Budnick *et al.*[15] and Preston *et al.*[16]

While we can explain the different temperature dependence of hyperfine field and magnetization by considering the CEP contribution of the hyperfine field only, the effects of lattice vibrations through s-d mixing to H_{CP} discussed by Butler *et al.*[2] may still be important.

In a recent publication[17] it was reported that the temperature dependence of the Gd hyperfine field in pure Gd displays an anomalous behavior. Figure 2 presents $(\sigma - h)/\sigma$ together with the lattice parameter c of the hexagonal Gd structure as functions of temperature. (The other lattice parameter a is approximately constant.) Unfortunately, neither the accuracy of the hyperfine-field measurements nor the temperature range of the lattice parameter measurements is yet sufficient for a detailed comparison of the data, but the agreement is qualitatively satisfactory.

A few simple applications of this semiempirical picture can be given. For example, the temperature dependence of the hyperfine field at a nonmagnetic impurity in alloys with a ferromagnetic metal differs from that of the matrix (e.g., Cu in Fe,[20] Sn in Fe, Co and Ni[21,22]). The deviation arises because, for a nonmagnetic impurity, the hyperfine field comes from the CEP contribution only, whose distance dependence, as well as the local thermal expansion $\Delta r(T)$ and lattice vibration $\langle x^2\rangle$ around the impurity, can differ from that of the pure matrix. The observed deviations in the temperature dependences for magnetic impurities such as V[23] and Co[24] in Fe, or Co[25] in Ni, for which the impurity-moment behavior is not anomalous, can be explained in a similar manner.

Detailed analysis of the pressure and temperature dependence of the shift for pure Fe and for dilute Fe in several alloys, as measured by the Mössbauer method, indicates[26] a temperature dependence of the isomer shift which cannot be accounted for by thermal expansion alone. We attribute the presence

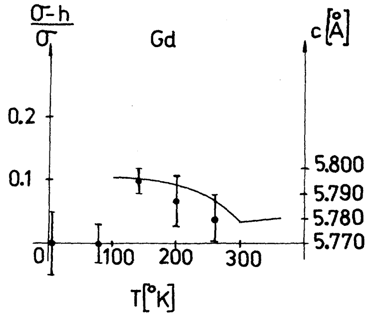

FIG. 2. Temperature dependence of $(\sigma-h)/\sigma$ at constant pressure for Gd. (Magnetization data were taken from Ref. 18, hyperfine-field data from Ref. 17, and the value of the lattice parameter c for the hexagonal Gd structure from Ref. 19).

of this explicit temperature dependence to the effect of lattice vibrations through a term proportional to $\langle x^2 \rangle$. A similar explanation can be given for the explicit temperature dependence of the hyperfine coupling constant of Mn^{++} and V^{++} in MgO and of Mn^{++} in several other cubic hosts.[27]

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ERRATUM

Effect of Band Structure on Spin Fluctuations in Nearly Antiferromagnetic Metals, M. J. Zuckermann [Phys. Rev. B 3, 3914 (1971)]. Professor Moriya has pointed out an error in my paper. The double density of states $N_q(\xi, \eta)$ given in Eq. (10) is incorrect to lowest order in the vector $(\vec{q} - \vec{Q}_0)$. The correct expression for $N_q(\xi, \eta)$ is

$$N_q(\xi, \eta) = \nu_0 \ln[\eta/(\eta - \tfrac{1}{2} q_c')] , \tag{1}$$

where

$$q_c' = \left| V_F(\vec{q} - \vec{Q}_0)_z \right| + [1/2(m_x m_y)^{1/2}] \left| (\vec{q} - \vec{Q}_0)_+ (\vec{q} - \vec{Q}_0)_- \right| \tag{2}$$

and

$$(\vec{q} - \vec{Q}_0)_\pm = (\vec{q} - \vec{Q}_0)_x \pm (\vec{q} - \vec{Q}_0)_y \; .$$

Since the transverse momentum component was neglected, Professor Moriya noted that $q_c' \equiv q' = |V_F(\vec{q} - \vec{Q}_0)_z|$, and q' must be replaced by q_c' [see Eq. (2a)] in Eqs. (10)–(24) and Eq. (27) in Sec. III of the paper. This invalidates Eq. (28) since the integral over momentum space in Eq. (27) becomes