Summary of Mössbauer evidence associated with the Kondo effect*

T. A. Kitchens
Brookhaven National Laboratory, Upton, New York 11973

R. D. Taylor
Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544
(Received 21 June 1973)

Mössbauer-effect measurements provided the first direct evidence of the reduction of individual effective localized moments on magnetic impurities with decreasing temperature. While other techniques such as magnetic susceptibility measure static collective properties, the Mössbauer and nuclear-magnetic-resonance techniques enjoy the capability of directly measuring the spin polarization within atomic dimensions of a given nucleus on a time scale of $\tau \sim 10^{-7}$–10^{-9} sec. Though the theoretical prediction of a reduction in the effective local moment for a simple and somewhat unrealistic Hamiltonian was made by Kondo some eight years ago and the theory reformulated, refined and improved, only phenomenological models have been developed to reduce the Mössbauer-effect data. In this note we analyze data for dilute Fe concentrations in several cubic transition metals for evidence of the reduction of the moments localized about Fe impurities. These results and others from the literature will be summarized and compared.

Early Mössbauer measurements on very dilute concentrations of ^{57}Fe in transition metals showed that noninteracting localized moments associated with Fe effectively decrease with decreasing temperature.[1,2] The Mössbauer technique determines the effective hyperfine field H_e at the nucleus;

$$\vec{H}_e = \vec{H}_0 + \alpha \langle \vec{\mu}(\mu H_0/kT) \rangle \ , \quad (1)$$

where $\vec{H}_0$ is the applied field, α is a constant dependent on the spin-polarization susceptibility at the nucleus and usually negative, μ is the magnitude of the local moment, and $\langle\vec{\mu}\rangle$ is the thermal average of the moment $\vec{\mu}$, at temperature T. Other small contributions to H_e, such as the Knight shift, are generally negligible. The internal field H_i is taken to be $\vec{H}_e - \vec{H}_0$. For an ordinary independent-spin system

$$\langle\vec{\mu}\rangle = (\vec{H}_0/H_0)\mu B_J(\mu H_0/kT) \ , \quad (2)$$

where $\mu = Jg\mu_B$ and $B_J(x)$ is the Brillouin function for spin J. g is the Landé factor usually equal to 2 in metallic systems and μ_B is the Bohr magneton. These early data were found to be quite consistent with a phenomenological model[2] in which the effective moment $\langle\vec{\mu}\rangle$ was reduced below the value expected from Eq. (2) by introducing a smearing field $\vec{s}$ whose fluctuations were fast compared with the hyperfine resolution time τ. It was assumed that this field $\vec{s}$ coupled vectorially with $\vec{H}_0$ and that the localized moment was always in thermal equilibrium with $\vec{H}_0 + \vec{s}$. Housley and Dash[3] have suggested a randomizing spin-density wave.[4] They show that for a spin-density wave spiraling about $\vec{H}_0$ Eq. (1) has a simple mathematical form which is consistent with data from Fe in Cu at 63 kOe.

As the concept of the reduction of the moment μ due to condensation into the spin-compensated state became clear,[5] data for Fe in Cu in fields up to 137 kOe were analyzed assuming

$$\mu \propto f(H_0, T) Jg\mu_B \quad (3)$$

where $f(H_0, T)$ decreases from 1 with decreasing T and increasing toward 1 with increasing H_0.[6] However, theoretical calculations[7] showed that the low-field susceptibility should be consistent with a Curie-Weiss form $\mu_e^2/(T+\Theta)$ for $T \gtrsim \Theta$, where Θ is related to the spin-fluctuation temperature in one formulation[8] or the condensation temperature in the other.[5] This suggests the form

$$\langle\mu\rangle = \mu B_J(\mu H_0/k(T+\Theta)) \ . \quad (4)$$

Maley and Taylor[9] have discussed this form, its justification, and the interpretation of Θ in more detail and have applied it to data for Fe in Mo. This form assumes that the spin polarizability at the Mössbauer nucleus remains constant and that the total localized moment decreases with temperature as $T/(T+\Theta)$ from its high-temperature value μ.

In Table I are shown the results of determining Θ, μ, and $H_{sat} = \alpha\mu$, with $g = 2.0$ from Mössbauer measurements of Eq. (1) using Eq. (4). The Mössbauer data were taken from Refs. 2, 6, 9, and 10, where details of sample preparation and experimental techniques can be found. New data were obtained as described in Ref. 2. The values of Θ, μ, and H_{sat} were found by applying a nonlinear minimization algorithm to

$$\chi^2 = \sum_j^n (\Delta H_{ij})^2/(n-3)\sigma_j^2 \ ,$$

TABLE I. Parameters of the hyperfine field of Fe^{57} in various hosts.

Host	$-H_{sat}$ (kOe)	μ (μ_B)	Θ (°K)	χ^2	$\bar{\sigma}$(kOe)	s values[a] (assuming $g=2$)
Au (Ref. 1)	190 ±2	3.2 ±0.3	1.1 ±0.1	1.8	4.5	1.8±1.4
Au (0.1-at.% Fe) (new)	175 ±2	3.4 ±0.2	1.4 ±0.1	0.81	3.3	
Au (Ref. 10)	206 ±4	3.0 ±0.4	1.0 ±0.3	0.29	9.4	
W (Ref. 2)	75.5 ±0.4	2.6 ±0.1	0.43 ±0.03	0.75	1.1	
Ag (Ref. 2)	36 ±2	3.8 ±0.5	1.7 ±1.1	0.72	2.9	4.4±0.4
Rh (Ref. 2)	131 ±15	4.6 ±0.7	13.1 ±1.0	1.4	1.5	13±3
Rh (1-at.% Fe) (Ref. 10)	47 ±4	9.0 ±1.0	5.7 ±3.1	0.15	2.0	
Mo (Ref. 9)	111.8 ±0.5	2.69 ±0.06	0.81 ±0.04	1.9	1.75	1.2±1
Mo (Ref. 9) $T>4$ °K	115 ±1	2.50 ±0.09	0.97 ±0.14	1.3	1.5	
Mo_9Nb_1[b] (new)	102 ±1	3.6 ±0.6	1.7 ±0.3	2.4	3.8	
Cu (Ref. 2)	85 ±19	5.1 ±1.6	26 ±2	0.82	0.9	18±3
Cu (Refs. 6 and 10)	96 ±16	4.1 ±1.0	27 ±2	0.38	2.9	
Cu (Refs. 2, 6, and 10)	82 ±8	5.3 ±0.7	26 ±1	0.40	2.3	

[a]Reference 2.

[b]R. D. Taylor (private communication).

where $\Delta H_i = H_i^{calc} - H_i^{meas}$. Both the minimum χ^2 and the mean deviation $\bar{\sigma}$ are given in the Table I to indicate the character of the fit. Though the errors in any data set are consistent relative to one another, the consistency between data sets is difficult to assess. This suggests that a relatively low χ^2 does not indicate excellent agreement with the form of Eq. (4) unless $\bar{\sigma}$ is also reasonably small, less than ~3–4 kOe.

The sufficiency of the form of Eq. (4) is well illustrated for these data, though data for $T<\Theta$ and also for $H_0 > k\Theta/\mu$ have been used. Corrections for increasing moment with applied field[11] were not employed, though if they were Θ would not be strongly affected from the data used here, as shown by the table entries for Mo. However more extensive calculations do show the same characteristics reported in Ref. 9. The results of this analysis and that of Ref. 9 are in strong disagreement with the interpretation of recent susceptibility measurements[12] which suggest that isolated Fe atoms in Mo have a moment of $2\mu_B$ with $\Theta = 30$ °K.

Comparison of the values of H_{sat} and Θ for Cu with the ones in the literature are in good agreement. For $T>20$ °K Heeger[13] reports $-H_{sat}=94$ kOe, $\mu = 3.7\mu_B$, and $\Theta = 32$ °K, while others find $-H_{sat} = 80 \pm 3$ kOe for isolated impurities.[6,14] Other analyses yield μ values as low as $2\mu_B$.[2]

Table entries for Rh and Au indicate the strong dependence of the parameters on Fe concentration. The experimental data, especially that for Au, indicate rather unique hyperfine fields suggesting that both clusters and isolated Fe sites do not coexist in these samples. The results for Au are in reasonable agreement with recent susceptibility measurements[14] which found that isolated Fe atoms in Au have a moment of $3.9\mu_B$ with $\Theta = \sim 1.5$ °K. For Fe atoms in Rh the situation appears to be more complicated. Nagasawa[15] finds the Curie-Weiss form insufficient to explain the data over the complete range of T. But allowing μ and Θ to be functions of T he finds for 0.72-at.% Fe in Rh $\mu \cong 2.0\mu_B$ and $3.5\mu_B$ with $\Theta \cong 7$ and 47 °K for $T=5$ and $\gtrsim 60$ °K, respectively. For Fe in Ir the same analysis is not applicable because the experimental range of H and T are such that the parameters μ and H_{sat} are not independent.[16] However, if either μ or H_{sat} is given any arbitrary value, Θ is well defined and extremely sensitive to Fe concentration, being $\sim 175\,^\circ K$ for ~ 0.07-at.% Fe and reducing to $\sim 64\,^\circ K$ for 0.1-at.% Fe.

Further comparison with Table I can be made with information presented in recent review articles.[7,13] Finally, we would like to point out that the analysis has not been applied to Fe in Pt and Pd but that the data[17] suggest Θ is definitely not zero but less than about $\frac{1}{4}\,^\circ K$.

*Work supported by the U. S. Atomic Energy Commission.

[1]R. D. Taylor, W. A. Steyert, and D. E. Nagle, Rev. Mod. Phys. 36, 406 (1964).

[2]T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. 138, A467 (1965).

[3]R. M. Housley and J. G. Dash, Phys. Lett. 10, 270 (1964).

[4]A. W. Overhauser, Phys. Rev. 128, 1437 (1962); J. Appl. Phys. 34, 1019 (1963).

[5]J. Kondo, Prog. Theoret. Phys. 32, 37 (1964); Prog. Theoret. Phys. 36, 429 (1966); Phys. Rev. 154, 644 (1967).

[6]R. B. Frankel, N. A. Blum, B. B. Schwartz, and D.-K. Kim, Phys. Rev. Lett. 18, 1051 (1967).

[7]Recent reviews have been written by M. D. Daybell and also by C. Rizzuto (unpublished).

[8]N. Rivier and M. J. Zuckerman, Phys. Rev. Lett. 21, 904 (1968).

[9]M. P. Maley and R. D. Taylor, Phys. Rev. 1, 4213 (1970).

[10]N. A. Blum, National Magnet Laboratory Report NML-64-2 (unpublished).

[11]Corrections for large H_0 have been calculated for $T = 0\,^\circ K$ by H. Ishii and K. Yosida [Prog. Theoret. Phys. 38, 61 (1967)].

[12]H. Claus, Phys. Rev. B 5, 1134 (1972).

[13]A. J. Heeger, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 283.

[14]B. Window, J. Phys. C Suppl. Met. Phys. XX, S323 (1970).

[15]H. Nagasawa, J. Phys. Soc. Jap. 25, 691 (1968).

[16]R. D. Taylor and W. A. Steyert, J. Appl. Phys. 37, 1336 (1966).

[17]M. P. Maley, R. D. Taylor, and J. L. Thompson, J. Appl. Phys. 38, 1249 (1967).