

accurate. However, if we express our results in the form (3.13) by changing $a(\varphi)$ we get the column for $\bar{a}(\varphi)$ in Table III. The values of $a(\varphi)$ given by (3.14) and evaluated with correct values of g_1 and g_2 are also tabulated there. It may be pointed out that only the transverse component of polarization can be detected experimentally, and $a(\varphi)$, in fact, serves as a measure of this transverse component.

If the incident beam is polarized transversely, with \mathfrak{P} along the x axis, and the scattered beam observed along $(\varphi, 0)$, we have

$$\begin{aligned}\pi_x(\varphi, 0) &= (|\mathfrak{P}|/2\pi)[e^{-s/4B}\varphi^{-1}g_2 + g_6 - \varphi^{-1}g_7], \\ \pi_y &= 0, \\ \pi_z(\varphi, 0) &= (|\mathfrak{P}|/2\pi)g_4.\end{aligned}\quad (3.15)$$

It is easily seen that the angle θ_T , by which the polariza-

tion vector is rotated, is equal to θ_L , discussed above. But for the azimuth $\psi = \pi/2$, we have

$$\begin{aligned}\pi_x(\varphi, \pi/2) &= (|\mathfrak{P}|/2\pi)[e^{-s/4B}g_1 - \varphi^{-1}e^{-s/4B}g_2 + \varphi^{-1}g_7], \\ \pi_y = \pi_z &= 0,\end{aligned}\quad (3.16)$$

there being no rotation of the polarization vector. Thus we see an azimuthal asymmetry in polarization, the angle θ_T decreasing from a maximum of $\theta_T = \theta_L$ at $\psi = 0$ to $\theta_T = 0$ at $\psi = \pi/2$. The degree of polarization τ_T for $\psi = 0$ is also tabulated, and also shows very little depolarization.

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Mössbauer Spectra of FeMo Alloys*

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Mössbauer spectra of FeMo alloys have been obtained for a series of closely spaced compositions from 2.1 to 6.0 at. % Mo. The hyperfine field and peak widths show a composition dependence suggestive of overlap of the disturbed surroundings of impurity atoms, in accord with results of neutron-diffraction studies of dilute impurities in iron. Analysis of the data in conjunction with the recent unpublished magnetization results of Aldred led to the deduction of a fractional increase in average iron magnetic moment, $(1/\mu_{Fe}) (d\mu_{Fe}/dC)$, of 0.25 per at. % and a magnetic moment per Mo atom of $0.4 \mu_B$ directed antiparallel to the iron moment, the latter value in good agreement with the neutron-diffraction results.

THE Mössbauer spectrum of iron alloys is complex and has been analyzed as the superposition of six-line spectra due to iron atoms in different local environments.¹⁻³ Approximate analyses have been made by assuming random distributions of the impurity atoms which reduce the hyperfine field (hf) of 1st, 2nd, ..., near neighbors by h_1, h_2, \dots , kOe. Wertheim *et al.*¹ represented the results of studies of several alloys by the equation

$$H(n, m) = H_{Fe}(1 + an + bm)(1 + kC), \quad (1)$$

giving the hf, $H(n, m)$, for an Fe atom with n impurity near neighbors and m impurity next-near neighbors in terms of $aH_{Fe} = h_1$, $bH_{Fe} = h_2$, and the constant k for

atomic concentration C . Stearns⁴ has extended this analysis to include the effects of 3rd- and 4th-neighbor impurity effects. Cranshaw *et al.*⁵ have emphasized the shortcomings of this simplistic approach and in their analysis of the spectra of FeSi alloys demonstrated the necessity for corrections due to local order, quadrupole splitting, and higher than first-order dependence on the number of impurity neighbors in a given shell.

In related experiments, Collins and Low⁶ have measured the magnetic-moment distributions around impurities in iron as evidenced in diffuse elastic neutron scattering. For elements to the left of iron in the Periodic Table (V, Mo, etc.), these workers found a small decrease on the moments of first and second neighbors of the impurity with a small increase in moment on the iron atoms at greater distance, the range

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¹ G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, *Phys. Rev. Letters* **12**, 24 (1964).

² M. B. Stearns, *Phys. Rev.* **129**, 1136 (1963).

³ T. E. Cranshaw, *Rev. Mod. Phys.* **36**, 395 (1964).

⁴ M. B. Stearns, *Phys. Rev.* **147**, 439 (1966).

⁵ T. E. Cranshaw, C. E. Johnson, M. S. Ridout, and G. A. Murray, *Phys. Letters* **21**, 481 (1966).

⁶ M. F. Collins and G. G. Low, *Proc. Phys. Soc. (London)* **86**, 535 (1965).

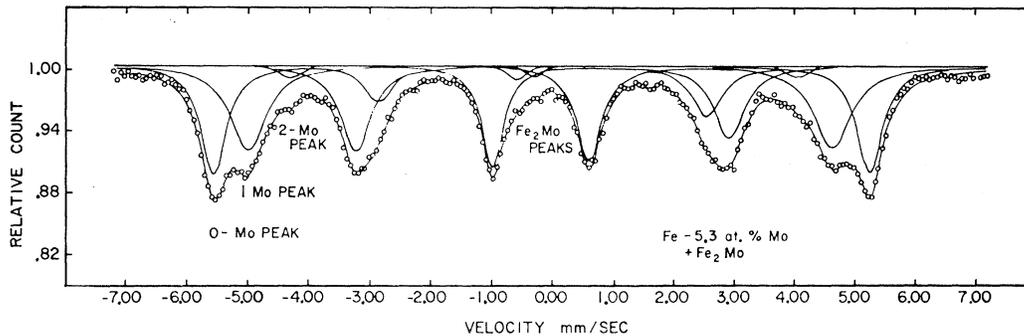


FIG. 1. Computer decomposition of the Mössbauer spectrum from Fe-6.0 at. % Mo as quenched from 1050°C and aged at 550°C for 820 h, corresponding to a matrix composition of 5.3 at. % Mo.

of the disturbance confined to a region of radial extent of 5–10 Å. In a reanalysis of the data of Collins and Low, Cambell⁷ has obtained a more detailed description of the magnetic-moment disturbance due to impurities. Bernas and Campbell⁸ have used these diffraction data to estimate ΔH , the weighted average of h_1 and h_2 in the Mössbauer results, in quite reasonable agreement with experiment for nine first and third transition series solutes in iron. Their analysis yields empirical constants relating the magnetic-moment disturbance to core polarization and conduction-electron contributions to the hf.

The present paper describes the results of a study of the Mössbauer spectra of FeMo alloys. The iron-rich portion of the FeMo phase diagram is characterized by a solubility as high as 26 at. % Mo at 1445°C rapidly falling to 1.14 at. % Mo at 550°C. In the course of studies of the precipitation of Fe₂Mo from supersaturated solid solution, described elsewhere,^{9,10} the Mössbauer spectra of various FeMo alloys were obtained. In analyzing the data, it was assumed that the observed spectra could be represented by the superposition of four simpler spectra; three six-line spectra due to iron atoms containing no Mo, one Mo, and two Mo atoms as first- or second-neighbor impurities, and one two-line (quadrupole split) spectrum due to the hexagonal precipitate Fe₂Mo. Lorentzian shapes were assumed for all lines. The details of this analysis and experimental procedure are described in Refs. 9 and 10. The satisfactory nature of this approximation is evidenced in Fig. 1 which shows the results for Fe-6.0±0.1 at. % Mo alloy as quenched from 1050°C and aged at 550°C for 820 h, corresponding to a matrix of composition 5.3 at. % Mo. From the areal ratios of the total absorption spectrum associated with the matrix relative to that of the precipitate, the matrix composition could be determined for samples annealed for various times at

various temperatures. In this analysis it is assumed that: (a) the precipitation does not result in an inhomogeneous matrix; (b) the Mössbauer fraction f is the same for iron atoms in the matrix and in Fe₂Mo. Assumption (a) is justified on the basis of electron microscopic evidence of homogeneous precipitation throughout the matrix for the relatively low temperatures and long annealing times used here, as well as by the agreement between results on alloys of the same *matrix* composition arrived at by different annealing paths. Assumption (b) has not been checked directly; however, it may safely be assumed that the Debye temperature for iron in the tightly bound Fe₂Mo intermetallic is not grossly different from that for iron in the matrix, and for 14.4-keV γ rays f is quite insensitive to small changes in the Debye temperature around 400°K. In any case, any small error here will introduce a constant multiplicative correction to the composition scale and not affect the results or their interpretation.

The areal ratios of the absorption associated with the "1-Mo peak" relative to that of the "0-Mo peak" agreed with those calculated for random solute distribution within 5% for all cases except the quenched

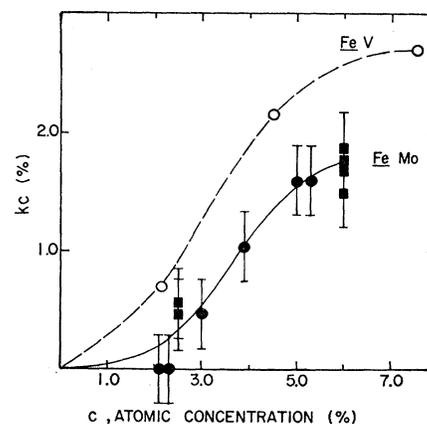


FIG. 2. Plot of kC versus atomic concentration [see Eq. (1)]. ■, alloys of indicated concentration rapidly quenched; ●, alloys of 6.0 at. % Mo quenched and annealed to give the indicated matrix composition; ○, data from Ref. 4.

⁷ I. A. Campbell, Proc. Phys. Soc. (London) **89**, 71 (1966).

⁸ H. Bernas and I. A. Campbell, Solid State Commun. **4**, 577 (1966).

⁹ H. L. Marcus, L. H. Schwartz, and M. E. Fine, Trans. Am. Soc. Metals **59**, 468 (1966).

¹⁰ H. L. Marcus, M. E. Fine, and L. H. Schwartz (unpublished).

alloys where quenching rate did affect the degree of local atomic order and hence the areal ratios to some small extent. (This explains, in part, the variability of the data for the 6 at. % alloy as shown in Fig. 2.)

The results are presented in Table I and in Fig. 2, and may be summarized as follows:

(1) The hf at an iron atom is reduced by 11.7% by the presence of one Mo atom as first or second neighbor [this number is a weighted average of the constants a and b in Eq. (1), and is equivalent to ΔH as used by Bernas and Campbell⁸].

(2) The data fit an equation of the form suggested by Wertheim *et al.*,¹ i.e., Eq. (1), with the exception that k is not independent of composition. The variation of the parameter kC is shown as a function of C in Fig. 2. The error bars represent twice the variation found in repetitive calibrations with the six-line spectrum of iron and thus somewhat overestimate the absolute error of any single point. In addition, Fig. 2 shows data for the parameter kC obtained by Stearns⁴ for V in iron. In both cases, a straight-line fit does not seem satisfactory indicating that k is not a constant. The curves are empirical, but suggest a saturation effect for compositions greater than 6 at. % solute.

(3) The experimental peak widths were only slightly larger for the 0-Mo peak than in pure Fe (see Table I), indicating a quite uniform environment for iron atoms farther than second neighbors from a solute Mo atom. For the 1-Mo and 2-Mo peaks, the peak width was much larger reflecting the expected small differences between h_1 and h_2 unresolved in this analysis. It is interesting to note that for both the 0-Mo and 1-Mo peaks the width increases and then decreases with concentration, indicating that in the concentration range where kC is changing rapidly there is more variability in the electronic configurations of the iron atoms than at very low concentrations or after saturation at high concentrations.

(4) Since this analysis averages the effects on iron atoms with Mo neighbors in first and second shells, little significance can be assigned to the isomer shift for the 1-Mo and 2-Mo peaks which varied in magnitude from -0.02 to -0.08 mm/sec relative to pure Fe in a nonsystematic way with composition. The isomer shift for the 0-Mo peak was 0.00 ± 0.01 mm/sec for all concentrations.

TABLE I. Hyperfine field and peak width as a function of molybdenum concentration.

Composition at. % Mo	Hyperfine field (kOe)		Peak width (mm/sec)	
	0-Mo peaks	1-Mo peaks	0-Mo peaks	1-Mo peaks
0	-330	...	0.30	...
2.5	-330 ± 1	-293 ± 1	0.40	0.39
5.0	-335 ± 1	-297 ± 1	0.48	0.87
6.0	-335 ± 1	-297 ± 1	0.38	0.65

The unusually large value of ΔH in the FeMo system increases the effective resolution of the Mössbauer spectra and enforces one's confidence in the analysis based on superposition of effects on the hf due to multiple near-neighbor impurities of an iron atom. Since no assumptions about the degree of local order were forced on the decomposition of the spectra, the agreement between the measured and calculated number of iron atoms with one and two near- and next-near-neighbor impurities confirms the assumption of random solute distribution in the matrix. Thus the FeMo system is ideal for revealing composition-dependent effects.

It is very attractive to interpret the term kC as reflecting the overlap of the regions of disturbed magnetic moment surrounding each solute atom as the concentration of solutes increase. This overlap would give rise to even more variability in iron-atom moments than that seen in the 1.5 at. % alloys examined by Collins and Low, as some iron atoms would simultaneously be in the disturbed range of one, two, or more solute atoms at various distances from the solutes. This is reflected in the increased peak widths in the composition range where kC is changing rapidly. When a concentration of 6-7 at. % is reached, one half of all the iron atoms have one near or next-near neighbor and all iron atoms are within the overlapping disturbed ranges of many solute atoms. At these concentrations all iron atoms with the same number of solute near neighbors would be expected to have the same average moment disturbance. This is once again reflected in the peak widths which narrow in this composition range. One would thus expect to see a much more uniform moment disturbance reflected in the diffuse elastic neutron scattering from more concentrated alloys, and indeed this is the case for alloys of 6 and 9 at. % V in iron.⁶ (The Mössbauer spectra of FeV show effects paralleling those seen in FeMo, see Fig. 2.)

The same value of kC for the 0-Mo, 1-Mo, and 2-Mo peaks reflects the fact that iron atoms with n -Mo neighbors are also within the disturbed ranges of other solute atoms. Thus the physical significance of k is related to the average fractional increase in iron magnetic moment. As shown by Johnson and Marshall,¹¹ in a matrix in which all iron atoms have identical electronic configurations the three primary contributions to the hf from the core s electrons, the conduction electrons, and the $3d$ electrons give effects proportional to the degree of polarization of the $3d$ electrons—i.e., to the magnetic moment of iron. A uniform change in the magnetic moment of iron would produce a uniform change in hf. It is thus tempting to interpret the uniform change in hf observed in alloys (kC) as reflecting a change in average iron moment—i.e.,

$$k = (1/\mu_{Fe}) (d\mu_{Fe}/dC). \quad (2)$$

¹¹ W. Marshall and C. E. Johnson, J. Phys. Radium **23**, 733 (1962).

The large change in hf for atoms with different environments (ΔH) is interpreted as due to *local* deviations in the conduction electron and core effects as described empirically by Bernas and Campbell.⁸

Assuming that the magnetic moment on the Mo atom is composition-independent, one obtains

$$\frac{1}{\mu_{\text{Fe}}^{\circ}} \frac{d\bar{\mu}}{dC} + 1 = \frac{1}{\mu_{\text{Fe}}^{\circ}} \frac{d\mu_{\text{Fe}}}{dC} + \frac{\mu_{\text{Mo}}}{\mu_{\text{Fe}}^{\circ}}, \quad (3)$$

where $d\bar{\mu}/dC$ is the change in average moment per atom as seen by saturation magnetization, and μ_{Fe}° is the magnetic moment of pure iron. Using Eq. (2), and combining the value of $k=0.25\pm 0.07$ for the composition of most uniform iron moment distribution, 6 at. % Mo, with the value of $d\bar{\mu}/dC = -2.10\pm 0.04$ determined for *FeMo* in the recent saturation magnetization measurements of Aldred,¹² one obtains $\mu_{\text{Mo}} = -0.4\pm 0.2\mu_B$ for the magnetic moment on the Mo impurity site, where the negative sign indicates a moment oppositely directed to that of the iron, and the quoted error is primarily associated with the error in k . This value for μ_{Mo} compares well with the neutron-

diffraction results of $-0.1\pm 0.6\mu_B$ (Ref. 6) and $-0.6\pm 0.6\mu_B$.⁷ If the iron atoms were assumed to carry an average moment of $2.22\mu_B$ independent of C , one would calculate $\mu_{\text{Mo}} = +0.1\pm 0.05\mu_B$ from the saturation-magnetization results.

A further comparison with the neutron-diffraction results can be made by using the empirical constants of Bernas and Campbell⁸ to calculate ΔH . The resultant $\Delta H/H_{\text{Fe}}$ for *FeMo* of 8.0% is in rather poorer agreement with the measured 12% than the other examples cited by Bernas and Campbell. This may be due to the fact that Campbell's analysis of the neutron-diffraction data for *FeMo* was made before the value of $d\bar{\mu}/dC$ became available and the derived moment distribution would be expected to be somewhat altered from the published results⁷ were this taken into account.

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¹² A. Aldred (private communication).

Jahn-Teller Effect of a d^1 Ion in Eightfold Cubic Coordination*

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The paramagnetic resonance of $\text{Sc}^{2+}(3d^1)$ exhibits three different kinds of spectra as the temperature is raised from 1.5 to 77°K. They are all explained in terms of internal asymmetry due to electronic-vibrational coupling (Jahn-Teller effect). Quantum-mechanical tunneling, as well as relaxation and strain, have an effect on the paramagnetic-resonance transitions. The first two effects are used to determine the symmetry and the energy level of the lowest vibronic states. From this an estimate of the parameters which describe the Jahn-Teller potential is made.

I. INTRODUCTION

THE dependence of paramagnetic resonance spectra of impurities in solids on the direction of the external magnetic field reflects the local symmetry near the impurity. For impurities substituting for lattice ions the local symmetry is very often the same as the crystal symmetry. This relationship is modified in two instances. First, another defect can be associated with the impurity. The resulting descent in symmetry is then found by considering all symmetry elements which leave both the impurity and the associated defect invariant. Second, the electronic state can be coupled to nuclear vibrations to yield a descent in symmetry. This much less obvious case is called the Jahn-Teller effect and is the subject of numerous

publications.¹⁻⁴ It is of importance only when the electronic state has an orbital degeneracy of two or more which arises from the crystalline field. Such cases have been investigated by paramagnetic resonance.⁵⁻⁷

Recently the system $\text{MgO}:\text{Cu}^{2+}$ attracted special interest. The ground state of $\text{Cu}^{2+}(3d^9)$ in octahedral coordination is Γ_3 . A theoretical study of d^9 ions in octahedral symmetry was undertaken by Bersuker

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⁴ M. C. M. O'Brien, Proc. Roy. Soc. (London) **A281**, 323 (1964).

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