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Mössbauer Studies of Au^{197} in Alloys of Gold with Transition Metals

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We have used the Au^{197} Mössbauer effect to study the properties of crystallographically ordered and disordered phases of Au_4V and Au_4Mn, and the disordered phase of Au_4Cr. The results show changes in the magnetic behavior of these systems due to disorder. Using the information from the Mössbauer experiments, a model is developed which can explain the complex magnetic behavior of the Au-V alloy system, which has been extensively studied recently. The model considers the V ions as having localized moments, as in the Anderson theory, and considers nearby transition-metal ions as perturbations on the *d*-state level width.

I. INTRODUCTION

THE Mössbauer effect[1] has proven a useful tool in metallurgical research in recent years.[2] Though most of the Mössbauer studies in metals have been done with the isotope Fe^{57}, many other metals have been used. With Au^{197} the useful information obtained from such experiments in alloys and intermetallic compounds comes mainly from two parameters: the hyperfine field (i.e., the magnetic field, H_{int} which the gold nucleus sees) in magnetically ordered materials; and the isomer shift (IS), a change in the nuclear-state energy levels due to the *s*-electron density at the nucleus. In most of the Au intermetallic systems studied to date, quadrupole hf coupling has been relatively small.

The primary source of the internal field in gold is the net electronic spin density at the nucleus resulting from the spin polarization of *s*-like conduction electrons by the exchange interaction with surrounding magnetic ions.[3] This spin density at the Au nucleus acts on the nuclear magnetic moment via the Fermi contact interaction, and can be considered equivalent to a magnetic field (H_{int}) at the nucleus. The net spin density reached in materials discussed here is only a few percent of the total *s*-electron density, so this source of H_{int} is far from being saturated. The field is then proportional to the strengths of the exchange interaction between the 6*s* electrons and the magnetic ions. Thus, for a particular surrounding, the internal field at the gold nucleus should be proportional to the moment of magnetic ions in the material, an assumption which is used here.

We also assume, only for the determination of the moment in Au_4V, that in isomorphous lattices with different 3*d* ions, H_{int} will be proportional to the 3*d* ion moment. This assumption essentially requires that the product of the 6*s* density at the Fermi energy and the exchange between the conduction and 3*d* electrons be constant in the different materials. This is only true to a good approximation. However, we note that the hf fields of gold dissolved in iron, nickel, and cobalt (which have different crystal structures), are accurately proportional to the host moment.[4] This is a severe test of the validity of the proportionality assumption.

From first principles, we can say very little about the IS expected for gold in transition metal hosts, but extensive measurements have been made[4,5,6] and we will use results of the earlier work in discussion of our data.

The main aim of this paper is to discuss magnetic properties and structure of Au_4M (M = Cr, Mn, V) alloys in the light of H_{int} and IS measurements.

Figure 1 shows a simplified nuclear decay scheme for the Au^{197} nucleus. The hfs to be expected for the Mössbauer transition used here consists of eight Lorentzian lines; with the intensities (under assumptions valid throughout these experiments) shown. Because the nuclear excited-state splitting is large compared to the ground-state splitting, the spectrum appears as two four-line groups. The relative splitting between the two groups and of the lines within the groups is fixed by the ratio of the nuclear ground-state to excited-state moments, which has recently been accurately determined.[5,7] For thin absorbers, the width of the individual Lorentzian lines can approach the natural linewidth (approximately 1.9 mm/sec, full width at half maximum), determined from the uncertainty principle using the known nuclear half-life of 1.8 ns. Thus, in cases where the interaction of the nuclear magnetic moments with H_{int} is the dominant cause of hfs, the observed spectra can be fitted using only H_{int} and the isomer shift as significant free parameters. To analyze the unresolved spectra obtained in some of these experiments, we assume that

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[1] R. L. Mössbauer, Z. Physik **151**, 124 (1958).

[2] See, e.g., reviews in *Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic Press Inc., New York, 1968).

[3] Contributions from 5*d* electrons are expected to be negligible both because they provide only small hf fields and because the 5*d* states lie about 2 eV below the Fermi surface. See, e.g., B. R. Cooper, H. Ehrenreich, and H. R. Phillipp, Phys. Rev. **138**, A494 (1965).

[4] L. D. Roberts and J. O. Thomson, Phys. Rev. **129**, 664 (1963).

[5] J. O. Thomson, P. G. Huray, D. O. Patterson, and L. D. Roberts, in *Proceedings of the International Conference on Hyperfine Interactions Detected by Nuclear Radiation*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968), p. 557; P. G. Huray, L. D. Roberts, and J. O. Thomson, *ibid.*, p. 596.

[6] Extensive Mössbauer spectroscopy in other Au-Mn alloys was reported by D. O. Patterson, L. D. Roberts, J. O. Thomson, and R. P. Levey, Oak Ridge National Laboratory Report No. ORNL-TM-1685 (unpublished); See, also, Ref. 5.

[7] R. L. Cohen, Phys. Rev. **171**, 343 (1968).

we know exactly the individual line shape and linewidth and the form of the hf interaction, i.e., the relative line intensities and positions, and this ignores three factors:

(1) An electric field gradient at the nucleus can result from asymmetric distribution of charge about the gold atom, and this gradient interacts with the nuclear quadrupole moment (see Fig. 1) to change the relative line positions. This effect is small for most of the gold compounds and alloys investigated to date. Since our measurements show that the linewidth (extrapolated to zero absorber thickness) for the ordered Au_4V phase above the Curie point approaches the theoretical value, it is safe to neglect the quadrupole hfs. Some additional support for this approximation is given by the fact that the hfs in the isomorphous Au_4Mn shows no quadrupole term, within small experimental error. Apparently, there is an accidental cancellation of the various contributions to the field gradient, since the symmetry about the gold site is too low to eliminate it.

(2) The thickness of the absorber tends to broaden the observed lines above the theoretical linewidth due to a saturation effect. (This is called "thickness" or "saturation" broadening.) This error is particularly difficult to account for because it is a function of (the absorber-area density)×(the recoil-free fraction)×(the "overlap" of the individual hf lines) and the last two factors vary rapidly over the temperature range used in these experiments. To ameliorate this problem, all our absorbers were made as thin as the preparation techniques allowed.

(3) Inhomogeneities in the absorbers (i.e., local disorder in the ordered phases) tends to broaden the lines and make the line shape non-Lorentzian. Since all our ordered-phase materials had close to the theoretical linewidth (when adjusted for thickness effects), this source of error should be small.

II. EXPERIMENTAL TECHNIQUES

Standard Mössbauer absorption spectroscopy techniques were used for the measurements. The source of the 77-keV γ rays was made by neutron irradiating[8] natural Pt metal to produce 2 mCi of the 21-h Pt^{197} which decays to Au^{197}. All isomer shifts given here are with respect to this Au in Pt source.[9] The Doppler modulation was provided by a standard loudspeaker-LVsyn velocity drive[10] with parabolic motion. The source was in the vacuum space in the Dewar, cooled to 20 or 4°K through a flexible copper reed attached to the bottom of the refrigerant container. The drive motion was brought into the Dewar by a glass push rod and bellows. The absorber holder in the vacuum space made thermal contact to the refrigerant container through a polyester heat leak. Its temperature was controlled by electrically heating it above the bath temperature. A differential thermocouple of Cu:Au-(2.1% Co) was used to measure and control the difference between sample and bath temperature.

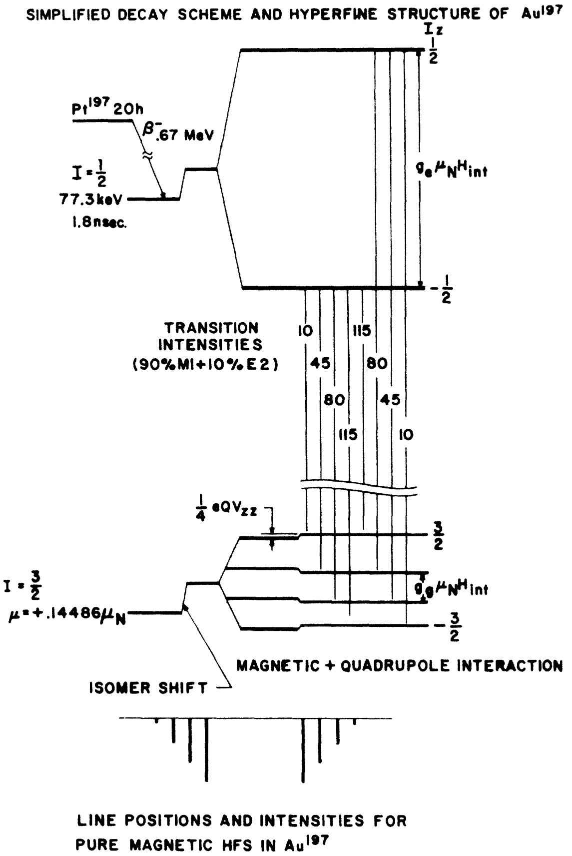

FIG. 1. Pertinent parts of the Au^{197} decay scheme and simple hf spectrum assumed for this work.

The γ rays were detected by a germanium detector and counted with standard instrumentation. A 400-channel analyzer operating in the time (multiscaler) mode was used to accumulate the spectrum. Count rates of approximately 30 000/sec were obtained with fresh sources.

A. Sample Preparation

The alloys were all made by arc melting together stoichiometric amounts of the appropriate metals on a water-cooled copper hearth. All starting materials were of greater than 99.95% purity. The arc melted "buttons" were sealed in evacuated quartz tubes and then homogenized at 1000°C for several days before order annealing at lower temperatures.

The Au_4Mn samples were annealed at various temperatures as discussed below, and then thick disks were sawn from the buttons. The disks were etched down in

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[8] The irradiations were performed at the Industrial Reactor Laboratory, Plainsboro, N. J.

[9] The IS of this source against pure Au was −1.24 mm/sec.

[10] R. L. Cohen, Rev. Sci. Instr. 37, 260 (1966); 37, 957 (1966).

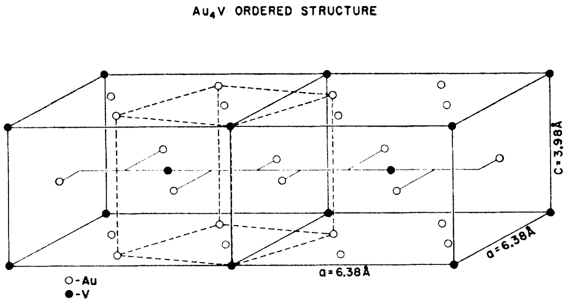

FIG. 2. Crystal structure of ordered-phase Au_4V and Au_4Mn after Ref. 15, isostructural with body-centered tetragonal Ni_4Mo.

aqua regia to remove a surface layer damaged during the cutting and to produce the final thickness (0.15 mm, about 175 mg/cm^2) used in most of the experiments. The Au_4Mn absorbers were checked by x-ray diffraction and reannealed at various stages to ensure that they were indeed in the desired phase; the ordered structure proved to be relatively insensitive to cold work. The intentional cold work (see Fig. 3) for studying the effect of disordering was done by rolling a sample that was initially 0.4 mm thick.

After homogenization, the Au_4V buttons were annealed at 500°C for one week to establish the ordered phase. After checking by magnetization measurements and x-ray diffraction to insure that the buttons had the Ni_4Mo structure, 0.4-mm-thick disks were spark cut from them. This completely eliminated the ordered phase as judged from magnetization measurements. The disk was then reannealed (with the original treatment) and etched to the 0.15-mm thickness used. Then it exhibited a magnetization of about 0.5 μ_B/(vanadium ion) at 1.5°K and 15 kOe, and a T_c of about 60°K, which was about as high as results obtained under these conditions in any other polycrystalline samples of this material.[11,12] The magnetization was also checked and found unchanged after the Mössbauer experiments were performed. A single sample was reannealed after rolling to 0.05 mm; the magnetization (and H_{int}) was found somewhat reduced on this sample, probably due to oxidation and incomplete ordering in the second anneal.

The Au_4Cr alloy was annealed at 300°C for four days; only the disordered fcc phase was observed by x-ray diffraction. The sample was cut from the button and etched to 0.15 mm. Judging from previous studies of the Au-Cr system,[13] the annealing temperature chosen may have been above the stability region of the Au_4Cr ordered phase. The Mössbauer spectra of our Au_4Cr samples were identical (within statistics) with those of the disordered Au_4V and presumably resulted from inhomogeneous IS (see below). These results will not be further discussed.

B. Results for $AuMn_4$

The results for the Au_4Mn samples are clear cut and will be discussed first.[6] Previous work[14] has shown that there are two forms of Au_4Mn: an ordered intermetallic with the Ni_4Mo structure (body-centered tetragonal, see Fig. 2), stable below 400°C, and an fcc form in which the Au and Mn atoms are randomly substituted for one another. Table I summarizes the important properties of these materials.

The Mössbauer absorption spectrum of the ordered phase (see the top of Fig. 3) can be fit perfectly under the assumption of pure magnetic hfs, with an H_{int} of 845±25 kOe, IS of +0.2 mm sec^{-1} (relative to the source of Au in Pt),[9] and a linewidth of 2.3 mm/sec. The line drawn through the data points is the spectrum predicted from the sum of the eight individual hf lines (see Fig. 1), spaced according to these parameters. It is seen to be an excellent fit to the data. The slight increase in linewidth over the theoretical minimum is due mostly to the absorber thickness (175

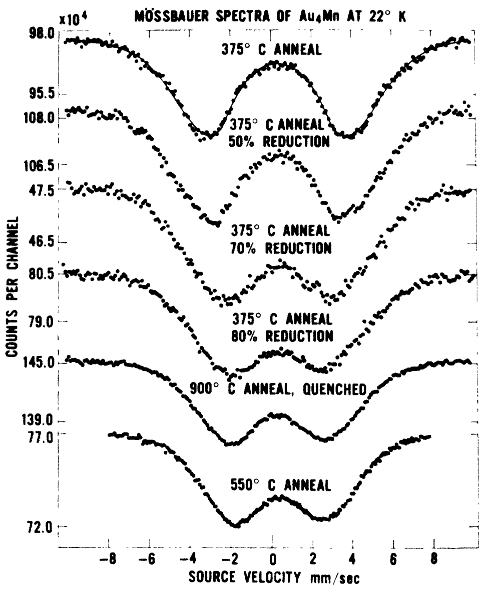

FIG. 3. Mössbauer spectra of Au_4Mn after various treatments of the material. [% Reduction = 100×(initial thickness − final thickness)/(initial thickness).] The uppermost spectrum is least-squares fitted (solid line), assuming pure magnetic hyperfine interaction, as described in the text. As the sample is disordered, the average hfs becomes smaller (as would be expected from the reduction of magnetic properties in the disordered material) and the splitting decreases. The lines are also somewhat smeared due to the presence of many different environments for the Au atoms.

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[11] A higher moment value has been obtained in high-field measurements by S. Foner (private communication).

[12] The fact that a value of 0.83 μ_B/(V ion) was obtained for an oriented sample shows that the magnetocrystalline anisotropy is extremely strong in this material. See G. Y. Chin, R. C. Sherwood, J. H. Wernick, D. G. Mendorf, and G. S. Knapp, Phys. Letters **27A**, 302 (1968).

[13] E. Wachtel and U. Vetter, Z. Metallk. **52**, 525 (1961).

[14] A. J. P. Meyer, J. Phys. Radium **20**, 430 (1959); Compt. Rend. **242**, 23 (1956); **242**, 15 (1956).

TABLE I. Pertinent properties of materials used in this work.

Material	Crystal structure	Magnetic ordering temp °K	Saturation moment[a] (μ_B per $3d$ ion)	Paramagnetic moment (p_{eff} per $3d$ ion, in μ_B)
Ordered Au_4Mn	Body-centered tetragonal	373[b]	4.15[b]	4.85[b]
Disordered Au_4Mn	fcc	203[b]	$<$4.15[b]	4.65[b]
Ordered Au_4V	Body-centered tetragonal	39[c] 59-66[d]	0.41[c] 0.83[d] 0.92[e]	1.5[c] 1.7[f]
Disordered Au_4V	fcc	$<$1.5[f]	~0	~0
Disordered Au_4Cr	fcc	~273[g]		
Ordered Au_4Cr	Body-centered tetragonal	~400[g]		

[a] Reference 21.
[b] Reference 14.
[c] See, L. Creveling, Jr., H. L. Luo, and G. S. Knapp, Phys. Rev. Letters **18**, 851 (1967).
[d] Reference 12.
[e] Reference 17.
[f] Reference 22.
[g] Reference 13.

mg/cm^2) and presumably, in small part, to slight differences in the local environment of the gold atoms.

This spectrum shows that the material is ordered magnetically and crystallographically and that all the Au nuclei experience the same size hf field. The fact that no electric quadrupole hfs exists is apparently accidental, since the symmetry about the gold atoms (only mirror symmetry exists) is too low to make the quadrupole splitting vanish identically. Au_3Mn, AuMn, and $AuMn_3$ also have symmetries which are too low to make the quadrupole splitting vanish, but have no significant quadrupole coupling.[6]

As expected, we could not fit the hfs of the disordered phase (shown at the bottom of Fig. 3) with a model assuming unique hf parameters for all Au nuclei. An analysis of the properties of the disordered Au_4Mn is in preparation and will be published separately.

It is possible to transform the ordered Au_4Mn phase to the disordered one by cold work. A series of hf spectra of samples with varying degrees of cold work is shown in Fig. 3. The spectra are seen to change essentially continuously; the results are consistent with the model of cold working destroying the long-range order locally (as in the recently proposed model for Au_4V)[15] and producing a range of environments for the gold atoms, resulting in broad lines. The over-all magnetic splitting is decreased somewhat by the disordering; this is consistent with observations[14] that the disordered state is "less magnetic" (i.e., has lower "ordering temperature" and smaller ordered moment per Mn ion) than the ordered one. In a forthcoming paper, we discuss how the reduction in magnetic behavior can arise from antiferromagnetic coupling between Mn ions which are nearest neighbors. The minor differences between the Mössbauer spectra of the 80% reduced material and the completely disordered phase presumably result from long-range order remaining in some regions of the sample, as would be expected from the nonrandom disorder produced by slip, as suggested in Ref. 15.

C. Results for Au_4V

The most significant result from measurements on ordered Au_4V is the determination of H_{int} at the gold nucleus. As stated previously, the small hf field in this material produces a spectrum consisting of only a broad line (see Fig. 4), and this must be analyzed with great care to extract a reliable value for H_{int}. Only the fact

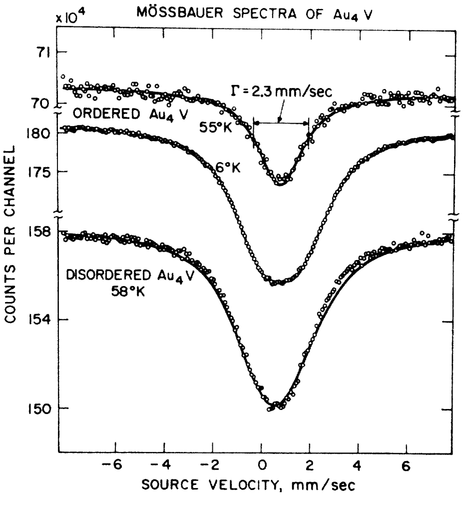

FIG. 4. Upper two curves show the spectra of samples of ordered Au_4V near the Curie temperature and at 6°K. The solid line through the 55°K data is a single Lorentzian of the width shown. The line barely visible through the 6°K data points is the result of a least-squares fit assuming pure magnetic hf structure. The curve through the disordered Au_4V points is the result of the "statistical IS" calculation discussed in the text. The calculated curve has been displaced about 0.5 mm/sec to the right to facilitate comparison of the calculated line shape with the data.

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[15] G. Y. Chin, J. H. Wernick, R. C. Sherwood, and D. R. Mendorf, Solid State Commun. **6**, 153 (1968).

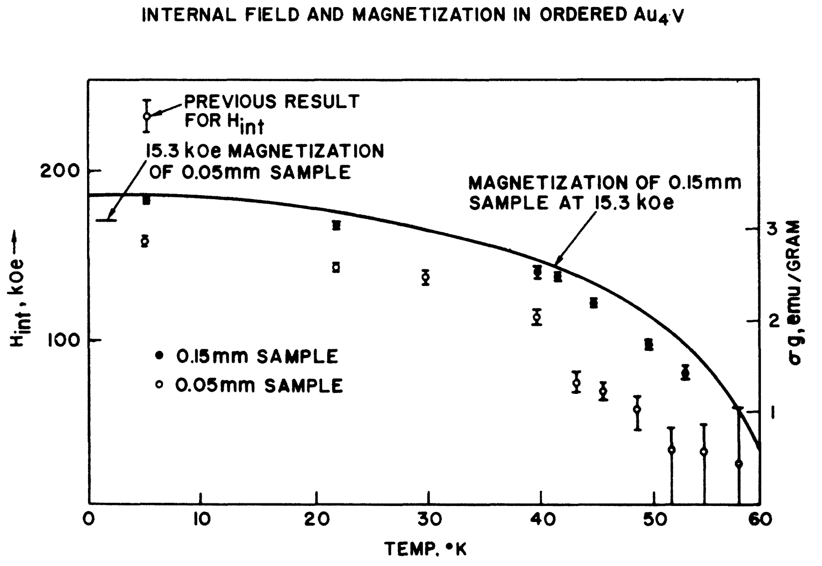

FIG. 5. Internal field and magnetization for Au_4V. The errors shown on the data points are 1σ statistical values only; more meaningful error limits are discussed in the text. The previous result plotted is that of Ref. 16.

that the hf interaction is describable using one significant parameter (i.e., the H_{int}) makes the analysis meaningful.

The Mössbauer spectra of this material (see Fig. 4) were analyzed (using the relative line spacings and intensities shown in Fig. 1) with a nonlinear least-squares program using as free parameters H_{int} and linewidth (assumed equal for all eight lines) plus the base line, over-all intensity, and IS. The data points and the least-squares curve are shown in Fig. 4 for a run with the 0.15-mm absorber at 6°K. The parameters corresponding to this curve are $H_{\text{int}}=185\pm25$ kOe, linewidth of 2.7 mm sec^{-1} (FWHM), and IS of 0.7 mm/sec relative to the source of gold in platinum. Similar analyses were done (using both fixed and variable linewidths) on spectra taken up to 55°K on various samples. From the results, we conclude that the increase in linewidth for the 0.15-mm sample (over the value 2.3 mm/sec shown in Fig. 4 for a 0.05-mm sample above the Curie temperature) is due partly to the increase in absorber thickness and partly to the increase in effective thickness resulting from the higher recoil-free fraction at low temperatures.

We observed distinct variations in H_{int} and linewidth among our samples. These could be correlated with measured magnetic moments and ordering temperatures as determined by bulk magnetization measurements. In general, samples that had relatively large magnetic moments and high ordering temperatures gave relatively large values of H_{int} and narrow linewidths. This presumably results from the fact that local disorder reduces the magnetic properties and broadens the Mössbauer lines. Both of these points will be discussed later. The value of $H_{\text{int}}=185$ kOe is that measured for the best sample as determined by magnetization measurements.

Measured values of H_{int} and magnetization for two samples of Au_4V are shown in Fig. 5. The hf field values for the 0.05-mm sample are of limited significance, since in this sample, the magnetic properties were decreased and the linewidth increased (presumably as a result of local structural inhomogeneities or oxidation occurring during the second anneal) from the values obtained for the best samples. This decreases the validity of the simple assumptions necessarily used in the analysis. These values represent very approximately a kind of average hf field over the gold nuclei. Also shown in Fig. 5 is an earlier measurement of H_{int}[16] by the same technique used here. We believe our results to be more accurate because of better sample preparation (as evidenced by higher T_c and Mössbauer lines of nearly the natural linewidth above T_c) and use of thinner absorbers to reduced error due to saturation effects.

III. DISCUSSION

The discussion can at this point be usefully divided into two parts. (1) Is crystallographically ordered Au_4V a normal ferromagnet with the magnetic properties primarily determined by localized $3d$ moments on the vanadium atoms? (2) If the ordered phase magnetic properties result from localized $3d$ electrons, why does the moment disappear in the disordered phase? The Mössbauer hf spectra help provide answers to both these questions.

The results of the measurements of H_{int} in the ordered-phase Au_4V point strongly toward the conclusion that its magnetic properties do indeed come from $3d$ electrons localized on the vanadium ions. We come to this conclusion by a comparison of H_{int} and

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[16] D. B. Dunlap, J. B. Darby, Jr., and C. W. Kimball, Phys. Letters **25A**, 431 (1967).

magnetic moments in the ordered Au_4V and Au_4Mn alloys. Preliminary reports of this have already appeared.[17] The authors of Ref. 16 reached a similar conclusion through less direct evidence.

As was discussed previously, H_{int} at the gold nuclei is a result of conduction-electron polarization resulting in a net electron spin density at the Au nucleus. Since these intermetallic compounds are isomorphous ferromagnets, one would expect the size of H_{int} to be proportional to the moment (if any) on the $3d$ ion. With the known value of the ordered Mn moment $4.15\mu_B$, the internal field of 845 ± 25 kOe (reported here) in Au_4Mn, and the value H_{int} $(Au_4V)=185\pm25$ kOe in Au_4V, we would expect $\mu=4.15\times185/845=(0.92\pm0.2)\mu_B$ for the V-ion moment in ordered Au_4V. (The error limits are arbitrarily chosen and reflect the possibility of deviations from the proportionality law.) Measurements of the paramagnetic susceptibility of Au_4V above the ordering temperature (see Table I) lead to results of $(1.4\text{–}1.7)\mu_B$, corresponding to an ordered moment of approximately 1 μ_B/V ion, consistent with this result. Direct magnetic moment measurements on polycrystalline samples of Au_4V have led to values of only about 0.5 μ_B/V or less; more recent results[12] of 0.83 μ_B/V in an oriented sample show, however, that the strong crystal anisotropy prevented magnetic saturation in the early work. Thus, the results of the Mössbauer and susceptibility measurements are consistent both with each other and with the local-moment model in which the magnetic properties come from the vanadium $3d$ electrons. If the observed bulk magnetization were produced by a spatially uniform conduction-electron polarization, fields on the order of 6000 kOe, 30 times larger than observed, would be produced at the Au nucleus. Thus it seems virtually impossible for the magnetic properties to result primarily from conduction electrons.

In fcc (crystallographically disordered phase) Au_4V, all the magnetic properties of the bct ordered phase seem to have disappeared (see Table I). The Mössbauer spectrum of this material remains essentially constant with temperature over the entire range from 4 to 58°K, the highest temperature measured. The width of the observed spectrum (see Fig. 4) is much broader than the theoretical value of 1.9 mm sec^{-1} expected for an unsplit line, indicating some form of temperature-independent hf interaction. The most obvious source of such an interaction is the IS. In the disordered alloy, the gold atoms have varying numbers of vanadium atoms as neighbors due to the random population statistics. The vanadium ions affect the electron density at the neighboring gold nuclei, and this results in a range of IS. We have calculated a spectrum based on a simple model using this assumption, and find good agreement (see Fig. 4) with the experimental results.

The details of the calculation are as follows: In the fcc structure, each gold atom as 12 nn atoms. Of these 12, on the average, 20% are V atoms and 80% are Au. The s-electron density increase (proportional to the IS) is assumed to be proportional to the number of nn vanadium atoms. (Gold with 12 gold nn's is assumed to lie at -1.24 mm sec^{-1} and an increase in IS of 0.53 mm/sec for each V nn has been used.) Then 13 Lorentzians of linewidth 2 mm sec^{-1}, heights obtained from the relative probabilities for 0–12 V nn's [readily calculated from the binomial distribution $(0.8+0.2)^{12}$], and IS proportional to the number of V nn's, are added together to produce the calculated spectrum. The differences between the observed and calculated spectra can be attributed to the oversimplification involved in considering just the first-neighbor shell.

The fact that the spectrum of the disordered alloy can be reproduced by this inhomogeneous IS model does not prove conclusively that this mechanism is the only significant source of hf interaction. It does show, however, that exotic effects do not have to be postulated to explain the Mössbauer results.

Thus, it appears that the moment on the vanadium ion does indeed disappear when the material is disordered, as would be expected from the lack of high-temperature paramagnetism. Any proper analysis of the ordered-phase magnetic properties must explain this effect.

The results of these Mössbauer experiments exclude the possibility that the vanadium moment disappears primarily because of promotion of its localized $3d$ electron(s) to an s-like conduction band in the disordered phase. If this were the case, the increased s-density would show up as an increased IS in the Mössbauer spectra, moving the center of the disordered-phase spectrum 1–2 mm sec^{-1} (toward positive velocity) from the ordered-phase peak position. The disordered phase spectrum is in fact (barely visible in Fig. 4) about 0.1 mm/sec toward positive velocity from the ordered-phase spectrum. This change is of the proper size and sign to be due to the decreased volume per atom (see Ref. 15) in the disordered phase, which, with a constant number of s electrons per unit cell, results in an increased s-electron density at the gold nuclei.

The results of the current experiments can be accounted for by the theory of localized magnetic states in metals proposed by Anderson.[18] This theory assumes the existence of localized d states, and uses a starting Hamiltonian involving the (Coulombic) repulsion among the d-electron wave functions and the s-d interaction as perturbations. The problem is solved exactly in the Hartree-Fock approximation, and the results pertinent to our analysis of the Au-V system are briefly as follows: The d-d Coulombic energy splits

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[17] R. L. Cohen, R. C. Sherwood, and J. H. Wernick, Phys. Letters **26A**, 462 (1968).

[18] P. W. Anderson, Phys. Rev. **124**, 41 (1961). A discussion of the application of this model to large impurity concentrations is being prepared by D. J. Kim, Phys. Rev. (to be published).

the available states for d-electron occupation into two virtual states, with the width of the states defined in terms of a parameter 2Δ, and U being the energy difference between the two states which can be characterized as spin up $(+)$ and spin down $(-)$. The localized d electron(s) fill the energetically lowest state. Since U is proportional to the occupation of one of these states, the preferential occupation of the lower state increases U, so that the energy splitting between the $+$ and $-$ states increases until all the d population is in that state. (This simplified discussion is borne out by self-consistent calculations described in detail by Anderson.[18]) The over-all result is that if U is large enough with respect to 2Δ, the localized d-state tends to have a large moment, since all of the d-electron population goes into one state. For a particular d population, the moment of the ion stays large as $U/2\Delta$ is decreased, but as the spin-up and spin-down states move closer together and begin to overlap, U is rapidly reduced (by the fact that both states are being populated). There is a critical value of $U/2\Delta$ below which, because of the self-consistent nature of the calculation, the magnetic state no longer exists and the spin-up and spin-down populations are equal. For us, the major result of this theory is that over a relatively small range of $U/2\Delta$, the ion changes from having a large moment to having no moment.

This is immediately applicable to explaining the loss of magnetization in the disordered Au_4V in the following way: If the V ions in Au_4V are near the region of "critical behavior" in terms of the Anderson model (in fact, it is generally believed that the magnetic properties of V in noble-metal hosts are explainable on this basis), a relatively small decrease of $U/2\Delta$ can result in complete loss of the moment on the V ion. If we hypothesize that the width of the d state 2Δ can be affected by the crystal field and that 2Δ is increased when the symmetry of the field decreases, we see that a loss of crystal symmetry about the V ion can result in complete loss of moment on the ion due to the decrease of $U/2\Delta$. This effect can explain most of the results observed in the work done on Au-V and on the Au-V-X ternary alloy to date. It has been pointed out[18] that not only the crystal field splitting but also a change in s density or the Fermi energy in the neighborhood of an impurity ion could cause the $3d$ ion to go from the magnetic to the nonmagentic state. Either of these other mechanisms would be a valid alternative to the crystal field perturbation we emphasize in the discussion here.

The analysis presented above allows many predictions of Au-V system behavior which can be compared with existing data. For example, in Au-V alloys in which the V ions are so dilute that they appear to have only Au neighbors, we would expect all the V ions to have large moments. As the V concentration is increased, the presence of V neighbors should eliminate the moment on some V ions, resulting in a decrease of "average apparent moment" per V ion. If x is the fraction of V atoms, the concentration dependence of the fractions of V ions still having a moment should look like the power function $(1-m)^m$, where m is the number of neighbors close enough to affect the d state width via crystal field effects. In the fcc gold lattice, $m=12$ if only nearest neighbors are considered important and $m=18$ for first- and second-nearest neighbors. In fact, extensive data published recently[19,20] roughly bear out this expectation in the range $x=0.5\%$ to $x=25\%$ for samples quenched from the melt to attain the maximum degree of disorder.[21] As the authors of Ref. 19 have shown, the fit of this power function to their data appears best for $m=18$ and a moment of $p_{\text{eff}}=1.7$–1.5, values consistent with what might be expected for our model for the completely disordered fcc system. The degree of approximation involved in our analysis, (particularly in that we assume that all the V ions have either the full moment or no moment, which is not the most general result of the Anderson model) can easily account for the discrepancies between model and theory. We should point out here that we differ from the authors of Ref. 19 only in that we suggest a specific mechanism for the loss of magnetic moment at high-V concentrations and accepting a p_{eff} of approximately 1.7 μ_B per magnetic V ion over the entire range of V concentration. The arguments presented here are also consistent with the results of Ref. 20, which also establish that V ions with V nn's have greatly reduced moments.

In another interesting experiment against which our model can be tested, the authors[22] studied the magnetic properties of the ordered alloys $Au_4V_{0.8}Nb_{0.2}$ and $Au_4V_{0.9}Ta_{0.1}$ (the Nb and Ta were assumed to replace V at random). In these materials, as can be seen from Fig. 2, each V atom has two V-site neighbors at 4.0 Å and eight at 4.8 Å. The Ta addition results in the reduction of p_{eff} from 1.7 μ_B/V (for pure Au_4V) to 1.6 μ_B/V in the alloyed material, a change which seems within the range of sample-to-sample variation reported in most work. If each V ion lost its moment when a Ta ion was at an nn V site, we would expect $p_{\text{eff}}=1.7$

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[19] L. Creveling, Jr., and H. L. Luo, Phys. Rev. **176**, 614 (1968).

[20] A. Narath and A. C. Gossard, Phys. Rev. **183**, 391 (1969); A. Narath, A. C. Gossard, and J. H. Wernick, Phys. Rev. Letters **20**, 795 (1968).

[21] In the discussion here, we have used only p_{eff} (high-temperature paramagnetic susceptibility) values as a measure of the V-ion moment, and have completely ignored moment values obtained from saturation magnetization measurements. Because of the extremely high magnetic anisotropy of these materials, saturation is not normally attained, and the reported moments are strongly dependent on the details of experimental technique. This undoubtedly is a major cause of the wide range of μ_B/V-ion values reported (see Table I). S. Foner (private communication) reports that even at an applied field of 150 kOe, the moment of Au_4V still increases with field. Additionally, we use the results of Ref. 19 for quenched samples, since those presumably possess the highest degree of disorder.

[22] H. Claus, A. K. Sinha, and P. A. Beck, Phys. Letters **26A**, 38 (1968).

$\times(1-0.1)^2=1.4\ \mu_B/\text{V}$, substantially smaller than the observed value. Thus, it appears that Ta neighbors are relatively ineffective in destroying the V moment. This is not unreasonable, since our explanation is based on crystal field effect and Ta is isoelectronic with V, and might be too small a perturbation on the pure Au_4V lattice to affect the width of the V *d* states. The Nb addition, on the other hand, reduces the average observed moment per V ion to 1.2 μ_B, close to the value $1.7\times(1-0.2)^2=1.1\mu_B$ that would be expected if the presence of a Nb ion at an nn V site completely destroyed the magnetic character of a V ion. Thus, very different arguments must be used to explain the results of diluting the Au_4V with Nb and Ta. This is unsatisfactory since Ta and Nb are isoelectronic and similar in size. A more reasonable argument would be that Ta and Nb are, in terms of the crystal field perturbations they produce, so much like V that they only reduce the V moment slightly. In fact, if we assume that the presence of a Ta or Nb ion 4.0 or 4.8 Å (the nn and nnn distance for V sites) reduces the V moment by 14%, a simple statistical calculation leads to expected average values for p_{eff} of 1.5 μ_B for the Ta-doped material and 1.3 μ_B for the Nb-doped material, not far from the experimental results. These arguments could be directly checked by additional measurements with samples containing different concentrations of Ta and Nb.

This model also directly explains, of course, the disappearance of the V moment in the disordered phase Au_4V; the crystal field effects resulting from the lack of site symmetry about the V ions directly result in loss of the magnetic properties. The destruction of the magnetic properties by dislocations (e.g., as introduced by spark machining) would also be explained in this way.

Additionally, we have performed the following test to establish the validity of the model: According to this mechanism, the susceptibility of a dilute alloy of V in Au should decrease with the addition of Nb, an element which is isoelectronic to V (and hence should look the same as a source of crystal field effects), but has no moment of its own. The decrease in paramagnetic susceptibility of the V ions as a function of Nb concentration should then show the effectiveness and range of the Nb ions in destroying the V moment.

A number of samples of Au doped with 2% V and, additionally, 2% and 4% Nb were made and their susceptibilities were measured. The results showed that the initial addition of Nb did substantially decrease the effective moments on the V ions, but that further additions had no effect. Careful metallographic analysis showed that regardless of the preparation technique used (high-temperature anneal, quench, or cold work followed by annealing), a Nb-rich phase was precipitated out, thus severely limiting the amount of Nb actually dissolved in the Au-V alloy. The results of the susceptibility measurements were in agreement with this analysis. (The phase diagram of the Au-V-Nb system has not been established.) We can consider it established that "magnetically inactive" ions in low concentrations (~1%) do decrease the V moments, but the quantitative behavior is unknown.

Thus, we see that essentially all of the many experiments done to date can be easily understood in the light of this relatively simple model, which assumes, as was stated: (1) That vanadium ions in gold are a marginal case for having local moments on the model proposed by Anderson, and that they have moments of approximately $p_{\text{eff}}=1.7\ \mu_B/\text{atom}$; (2) that crystal field effects from nearby nongold ions can reduce or eliminate the moments on the V ions.

IV. SUMMARY AND CONCLUSIONS

In this paper we have discussed the magnetic properties of the ordered and disordered Au_4V and Au_4Mn alloys in the light of previously published susceptibility and magnetization studies. By combining the previous work with the results of Mössbauer-effect experiments presented here, we were able to arrive at a microscopic model, based on the Anderson local-moment model which describes the complex behavior of the Au-V alloy system. This picture appears to be in accord with both the previously published magnetization results and our own Mössbauer and magnetization data.

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