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Magnetic Properties of Gold-Rich Gold-Vanadium Alloys*

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Results of measurements on Au–V alloys are presented. The intermetallic compound Au_4V, formed through an order-disorder transformation at 560°C, becomes ferromagnetic at ≈ 60°K. Above that temperature the susceptibility satisfies a Curie-Weiss law. The induced moment at absolute zero, the effective moment, the transition temperature, and the temperature-independent component of the susceptibility all vary from sample to sample, but typical values are $0.5\mu_B$ per V ion, 1.7, 50°K, and 150×10^{-6} emu/(g at. wt), respectively. The variation is thought to be due to extreme magnetic hardness coupled with a high degree of crystal imperfection. All results indicate that a model of localization in the molecular-field approximation is adequate to describe the ferromagnetism. In agreement with earlier work, dilute solid solutions of V in Au have temperature-dependent susceptibilities. The susceptibilities are describable by a Curie-Weiss law, with parameters that vary with concentration and heat treatment. Temperature dependence occurs only in the concentration range ≈ 0.1 to 30 at.% V; the Curie constant reaches a maximum value at 5–10 at.% V. A model is presented which can account for the results observed by assuming that a V ion localizes in Au only if there are no V neighbors within a critical distance. In conclusion, the implications for the possible existence of other ferromagnetic intermetallic compounds are discussed.

1. INTRODUCTION

In this paper, the magnetic properties of gold-rich, gold-vanadium (Au–V) alloys measured between 0.4 and 293°K are reported. First, a brief review of previous work is given. Then the experimental results are presented and possible interpretations are discussed. A simple statistical model is proposed which relates the magnetism of solid solutions to the ferromagnetism of Au_4V. Finally, the implications for the possible existence of other ferromagnetic intermetallic compounds are discussed.

2. SYSTEM

Investigations of various parts of the Au–V alloy system have been reported by several authors[1–6] and the phase diagram is well determined. Shown in Fig. 1 is a part of this diagram (from 0 to 50 at.% V) which is reproduced from Ref. 4 with modification of the Au_4V order-disorder transition phase boundary proposed in Ref. 6. The two intermetallic compounds are both formed through order-disorder transformations. Au_4V has a tetragonal structure isotypic with Ni_4Mo ($D1_a$) and its lattice parameters are $a=6.40$ Å and $c=3.98$ Å. The crystal structure of Au_2V has not yet been determined.[4,5] The solid solubility extends to about 50 at.% V at 1000°C; this makes the system an exceptionally favorable one for investigation.

3. PREVIOUS WORK

The first published magnetic data on the system is that of Vogt and Gerstenberg (1959).[7] They measured five samples, ranging in concentration from 1 to 15 at.% V, over the temperature interval 90 to 900°K. They found that the susceptibility χ in each case consists of two parts, one temperature-independent and the other satisfying a Curie-Weiss law with negative critical temperature. There is, however, no indication of a transition in χ at the corresponding temperature. All the parameters are concentration-dependent. To describe their results they assumed that a fraction (decreasing with increasing V concentration) of the V ions have localized magnetic moments (hereafter referred to as magnetic); these generate the Curie-Weiss component, and the remainder contribute to the temperature-independent part of χ. No explanation was offered for the negative critical temperature.

In 1964 Lutes and Schmit[8] published their work on dilute alloys of V, Cr, Mn, Fe, and Co in Au. The work was primarily concerned with Cr, Mn, and Fe; they reported but one Au–V sample (1 at.% V) measured between 0.52 and 10°K.

Recently, Kume (1967)[9] reported measurements on four alloys, varying in composition from 0.3 to 2 at.% V, over the range 1.4 to 1000°K. He assumed that all the V ions have localized magnetic moments, but that these are partially compensated by conduction electrons of opposite spin through an antiferromagnetic *s-d* exchange interaction (the Kondo effect). Hence, χ at any given temperature is less than the uncompensated (Langevin)

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* Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 631-67.

† Also Department of Applied Electrophysics.

[1] D. Summers-Smith, J. Inst. Metals **83**, 189 (1954–1955).

[2] E. A. Wood and B. T. Matthias, Acta Cryst. **9**, 534 (1956).

[3] H. Warlimont, Z. Metallk. **50**, 708 (1959).

[4] W. Köster and H. Nordskog, Z. Metallk. **51**, 501 (1960).

[5] E. Stolz and K. Schubert, Z. Metallk. **53**, 433 (1962).

[6] W. Köster, H.-P. Kehrer, and P. Rothenbacher, Z. Metallk. **54**, 682 (1963).

[7] E. Vogt and D. Gerstenberg, Ann. Physik **4**, 145 (1959).

[8] O. S. Lutes and J. L. Schmidt, Phys. Rev. **134**, A676 (1964).

[9] K. Kume, J. Phys. Soc. Japan **22**, 1309 (1967); K. Kume, Phys. Letters **24A**, 743 (1967); K. Kume, Tech. Report of the Institute for Solid State Physics ISSP, Univ. of Tokyo, Ser. A, No. 267 (1967).

value. Moreover, the compensation increases with decreasing temperature so that the deviation in χ increases also. Thus he could account for the temperature dependence and, more significantly, the negative critical temperature. Having assumed, however, that all the V ions are magnetic (and making the additional assumption that the Au matrix is unaffected magnetically by the V), Kume took the temperature-independent part to be equal to the value for pure Au. This meant that the temperature-dependent part satisfied a Curie-Weiss law only at the lowest concentration (0.3 at.% V).

Figure 2 shows all the susceptibility measurements reported to date, incorporated with part of the data reported in this paper. In view of the fact that the value of χ for a given sample depends to a certain extent on its heat treatment (to be discussed in Sec. 5 B), the agreement is quite satisfactory, except for the Lutes and Schmit sample. More will be said about the comparison at the appropriate point.

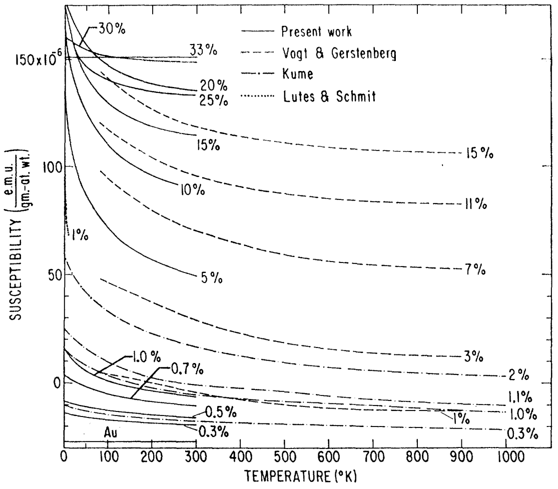

FIG. 2. Susceptibility of disordered solid solutions versus temperature for various concentrations. The concentrations are given in at.% V.

4. EXPERIMENTAL DETAILS

The samples were prepared from 99.97% pure V and 99.999+% pure Au obtained from Materials Research Corp. and American Smelting and Refining Co., respectively. According to the spectrographic analyses supplied by the manufacturers, the magnetic impurity level (including Cr, Mn, Fe, Co, and Ni) is less than 35 ppm in V and 3 ppm in Au.

The alloys were prepared by arc-melting proper amounts of the elements under an atmosphere of purified argon. There followed four distinct types of heat treatment:

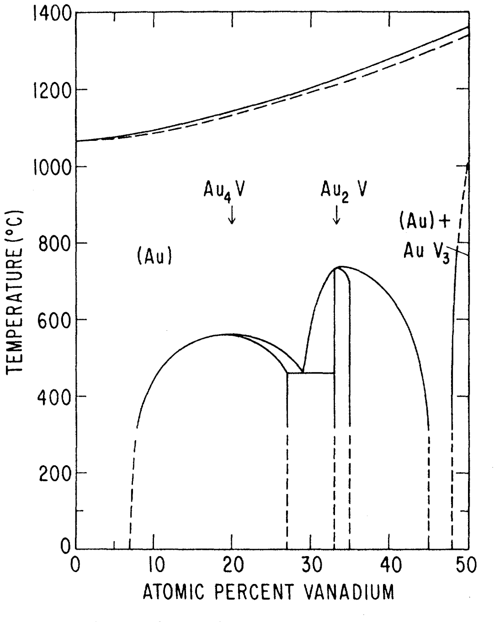

FIG. 1. Part of the phase diagram for the Au–V alloy system. All phase boundaries below 300°C have been indicated as uncertain (dashed) for reasons given in the text.

(1) Splattered (s)—The sample was prepared by the technique of quenching from the liquid state adapted to an arc furnace.[10] This was done in order to preserve the (presumably) completely random distribution of V ions in the molten alloy.

(2) Homogenized (h)—After arc-melting, the sample was sealed in a quartz tube under a reduced helium atmosphere and heated at 1000°C for from three to five days. At the end of this time the quartz tube containing the sample was removed from the furnace and quenched in water at room temperature.

(3) Heat treated (ht)—After homogenization, the sample underwent the following heat treatment: held at 500°C for 15 days, then at 400°C for 35 days, finally at 350°C for 8 days.

(4) Annealed (a)—The ferromagnetic samples were held at 500°C for from 4 days to 2 months following homogenization. Two were then kept at 300°C for 15 days.

Alloy heat treatments were all of these four general types unless otherwise stated. Hereafter, the terms "splattered," "homogenized," "heat treated," and "annealed" will be used in the special sense described above. After melting and after each stage of heat treatment (except for the splattered samples) the samples were reweighed. The weight losses were always negligible (usually less than 0.05% and always less than 0.4%). Just prior to making the magnetic measurements (again excepting the splattered samples) the samples were rinsed in dilute hydrochloric acid to remove surface magnetic contamination.

Crystal-structure determinations were made by means of the x-ray powder technique with Cu $K\alpha$

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[10] H. L. Luo, J. Less-Common Metals 15, 299 (1968).

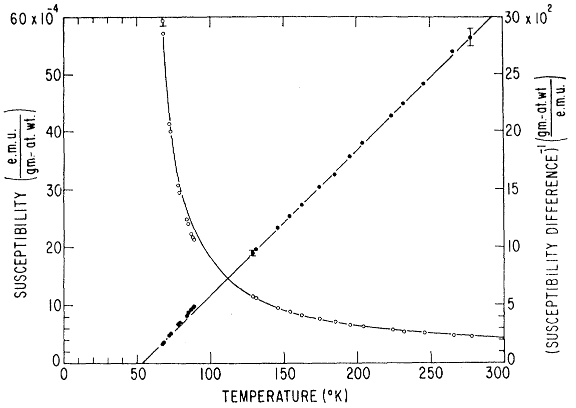

Fig. 3. Susceptibility (open points) and reciprocal susceptibility difference $(\chi-\chi_0)^{-1}$ (solid points) for sample No. 5(1) showing the Curie-Weiss behavior above the transition temperature.

radiation from filings taken from the samples after the magnetic measurements had been made. The filings had to be heat treated again to eliminate the effects of the cold work caused by filing. The results are discussed at the appropriate points in the text.

The magnetic measurements were made using the Faraday method in a cryostat that is described elsewhere.[11] Measurements can be made from 0.37 to 293°K in fields from 0 to 11 kOe. The limit of sensitivity is approximately 2×10^{-5} emu for the moment or 1×10^{-7} emu per g at. wt for χ. There are two groups of experimental errors, random (uncertainty from point to point in a measurement on one sample) and absolute (uncertainty in the absolute value). The error bars on figures represent only the random component (except for the reduced moment plots; for these, error bars represent total error). The absolute error for splattered samples is about 75% of the random error; for all others it is about 15%. In both cases a lower limit of about 1% of the measured value is estimated. The error bars on the reciprocal plots diminish rapidly with decreasing temperature, so that often they are not plotted except for a point close to room temperature. They do not include the error in the subtracted part, χ_0 (see Sec. 5 B 1).

5. EXPERIMENTAL RESULTS

A. Ordered Au_4V

1. *Main Results*

Ordered Au_4V undergoes a ferromagnetic transition[12] at about 60°K. Above the transition temperature T_c, the susceptibility χ obeys a Curie-Weiss law (Fig. 3), $\chi=\chi_0+C/(T-\theta)$, where χ_0 is the temperature-independent component of χ, C is the Curie constant, T is the temperature, and θ is the critical temperature. Below T_c, the magnetization is typical (Fig. 4). The magnetization was measured on several samples in external fields ranging from 800 to 11 000 Oe. The induced magnetization was independent of inducing field up to about 5°K below T_c. There is very little variation in the reduced magnetization $[M(T)/M(0)]$ as a function of reduced temperature (T/T_c) even though the magnetization at 0°K $[M(0)]$ and T_c do vary considerably from sample to sample. This is shown in Fig. 4(a), where reduced moment plots for seven samples are superimposed. [Reduced moment$\equiv$ $\mu(T)/\mu(0)$ = reduced magnetization.] A hysteresis loop

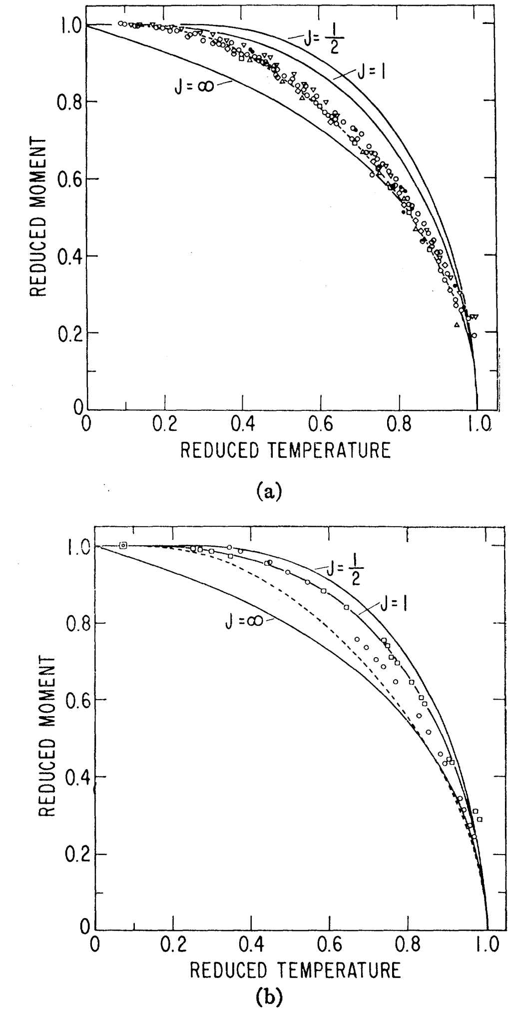

Fig. 4. Reduced moment versus reduced temperature (i.e., normalized to the moment at absolute zero and the transition temperature, respectively) for (a) seven samples (differentiated by different symbols) and (b) one sample (No. 5) measured twice with the two orientations perpendicular (the circles are one measurement, the squares the other). The dashed line represents the composite in Fig. 4(a) and is reproduced in Fig. 4(b). The solid lines are the molecular-field-theory predictions for angular momentum J, $=\frac{1}{2}$, 1, and ∞.

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[11] D. K. Wohlleben, Ph.D. dissertation, University of California, San Diego, 1968 (unpublished).

[12] L. Creveling, Jr., H. L. Luo, and G. S. Knapp, Phys. Rev. Letters **18**, 851 (1967).

TABLE I. Data on Au_4V and Au_4V-based substitutional alloys.

Sample[a]	Concentration α (at.% V)	Heat treatment[b] (Number of days at 500°C)	χ_0[c] $\left(\frac{10^{-6}\text{ emu}}{\text{g at. wt}}\right)$	C[d] $\left(\frac{10^{-3}\text{ emu °K}}{\text{g at. wt}}\right)$	p[e] (μ_B)	θ[f] (°K)	T_c[g] (°K)	$\mu(0)$[h] (μ_B)	q_c/q_s[i]	Molecular-field approx. result:
1a	19.80	4	252	55.5	1.49	41	44	0.41	1.91	1.51
1b		7[j]					50	0.43		1.51
1c		13	311	48.6	1.39	41	44	0.41	1.73	1.55
2a	20.00	19	134	64.3	1.58	49				
2b		19	134	30.6	1.09	49	52	0.47	1.02	
3	20.00	28					45	0.38		
4a	20.03	7	195	47.3	1.36	44				
4b(1)		7	110	58.1	1.51	48				
4b(2)			144	69.6	1.65	44	45	0.43	2.16	1.35
4c(1)[k]		7					47	0.36		1.70
4c(2)[k]							47	0.37		1.68
5(1)[l]	20.00	45[m]	95	79.7	1.76	53	59	0.60	1.70	1.78
5(2)[l]							57	0.52		2.18
6	17.01	7					30	0.20		
7a	18.99	7	119	48.4	1.38	47				
7b		7					45	0.29		0.99
8a	22.03	7	165	42.7	1.29	40				
8b		7					46	0.31		1.68
9a	24.01	7	41	67.5	1.63	40				
9b		7					47	0.26		1.93
10	20.03[n]	11	377	43.5	1.31	43	46	0.36	1.81	1.55
11	20.03[o]	14[m]	4	96.1	1.94	51	58	0.42		1.18

[a] The letters in the sample designations indicate different pieces of the same ingot. The bracketed numbers indicate different runs with the same piece.

[b] See Sec. 4.

[c] Temperature-independent component of the susceptibility χ.

[d] Curie constant. $C \equiv (N_A p^2 \mu_B^2)/3k$, where N_A is Avogadro's number and k is Boltzmann's constant.

[e] Effective moment per vanadium ion as obtained from C.

[f] Paramagnetic critical temperature.

[g] Critical, or transition, temperature as determined by the appearance of remanence.

[h] Induced moment per vanadium ion at absolute zero. It was measured for most samples at 4.3°K, but measurements on some samples at 0.37°K showed no change from the 4.3°K value.

[i] These quantities are defined, where necessary, and discussed in Sec. 5 A 4.

[j] Cold worked before heat treatment.

[k] The direction of orientation for one measurement was perpendicular to that for the other.

[l] Same as k.

[m] Followed by 15 days at 300°C.

[n] Au_4V plus 0.1 at.% Fe.

[o] Au_4V plus 2.25 at.% Fe.

is shown in Fig. 5. It was measured at a temperature close to T_c. Even here the coercive field is considerable, and at 4.2°K it is much larger than the maximum available field (11 000 Oe). At that temperature, completely reversing the field causes only a few percent decrease in the magnetization.[13] The pertinent data on several samples is summarized in Table I.

2. *Anisotropy and Crystal Imperfection*

An examination of the above results indicates that Au_4V is a highly anisotropic ferromagnet. Anisotropy accounts for its extreme magnetic hardness. Evidently, 11 000 Oe is sufficient only to cause magnetization in the "easy" direction closest to the field direction, but insufficient to cause domain magnetization rotation. Such anisotropy is not surprising in view of the crystal structure; the V ions form a body-centered tetragonal (bct) lattice of dimensions 4×6.4×6.4 Å.

Several experimental results suggest a high degree of crystal imperfection. Chin *et al.*[14] have discussed this and point out that because the *c* axis of the bct (ordered Au_4V) cell can be aligned with any one of the three equivalent axes of the fcc (disordered Au_4V) cell, a polycrystalline sample will not only have variations in crystal orientation from grain to grain, but also crystal imperfections within a grain. Coupled with the sensitivity of spin localization to spacing (see Sec. 6), this can account for the rather wide variation in parameters

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[13] If the sample is cooled in zero field to 4.2°K the magnetization is perfectly linear and reversible at that temperature. This in fact happened to us with our first ordered sample, to our surprise (see Ref. 39 below); it was not until the temperature was increased to about 20°K that the magnetization became nonlinear and hysteresis began to appear. Because of this it was necessary to collect subsequent data below the transition temperature by cooling from above it in a nonzero magnetic field.

[14] G. Y. Chin, J. H. Wernick, R. C. Sherwood, and D. R. Mendorf, Solid State Commun. **6**, 153 (1968). Note especially the micrograph of ordered aud disordered Au_4V.

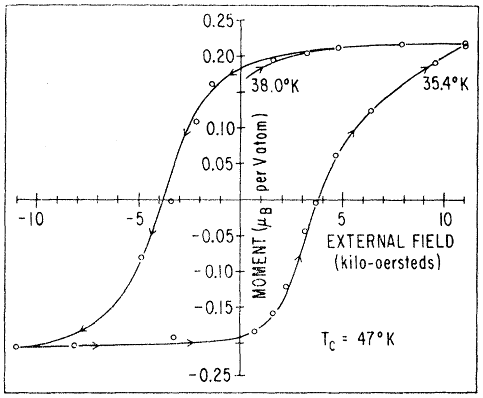

FIG. 5. A hysteresis loop showing the induced moment versus the external magnetic field. The temperature was 38.0°K at the beginning of the measurement and 35.4°K at the end. The transition temperature for the sample is 47°K.

from sample to sample listed in Table I. Note especially the variations in χ_0 [$(95\text{–}311)\times10^{-6}$], the effective moment p [1.09–1.76], and θ [41°–53°]. These are obtained from data measured above T_c, where anisotropy is not a factor. Crystal imperfection would result in variations in the effective exchange parameter and the number of magnetic ions, however, causing variations in the parameters mentioned above as well as in T_c and magnetization. In this regard, Fig. 4 is of particular interest. It shows that reduced moment as a function of reduced temperature is universal. This is to be expected since the dependence on degree of crystal imperfection has been removed in the normalization of the two quantities.

Further evidence for crystal imperfection is provided by the large residual resistivity,[15] and the negligible change in the moment of a sample when run in mutually perpendicular directions (see data in Table I on sample Nos. 4c and 5). The moment should certainly be different in this case because of the anisotropy (especially for sample No. 5, which was made up of only 2 or 3 grains).[16] Finally, crystal imperfection may account for the "smeared out" nature of the specific-heat anomaly.[17]

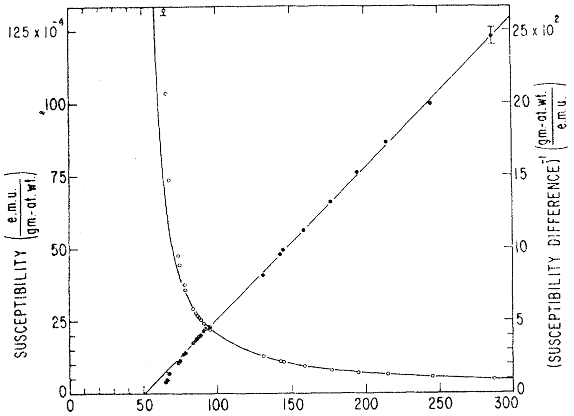

FIG. 6. Susceptibility (open points) and reciprocal susceptibility difference $(\chi-\chi_0)^{-1}$ (solid points) for the iron-doped sample (2.25 at.% Fe), No. 11.

3. *Effect of Heat Treatment, Stoichiometry, and Impurity Level*

The above-described effects do not appear to be caused by heat treatment, stoichiometry, or impurity level. The samples summarized in Table I were subjected to widely varying heat treatments; there is little or no correlation with p, T_c, or $\mu(0)$. Sample Nos. 7, 8, and 9 show the effect of stoichiometry. p and $\mu(0)$ generally tend to decrease as the concentration diverges from 20 at.% V, but only gradually, in agreement with the broad concentration range of the ordered phase. Sample Nos. 10 and 11 show the effect of adding Fe impurities. Within the rather broad range of values for each parameter, addition of 0.1 at.% Fe (1000 ppm, well above the impurity levels in the constituents) has no effect. The addition of 2.25 at.% Fe (about 10% of V content) has little effect; it mainly acts to increase C. Figure 6 shows χ and the reciprocal of the susceptibility difference $(\chi-\chi_0)^{-1}$, and Fig. 7 shows reduced moment versus reduced temperature for this sample (No. 11). As a crude estimate of the contribution of the Fe to C, assume a contribution of 65×10^{-3} by the Au$_4$V to C. Then the Fe contribution must be about 30×10^{-3},

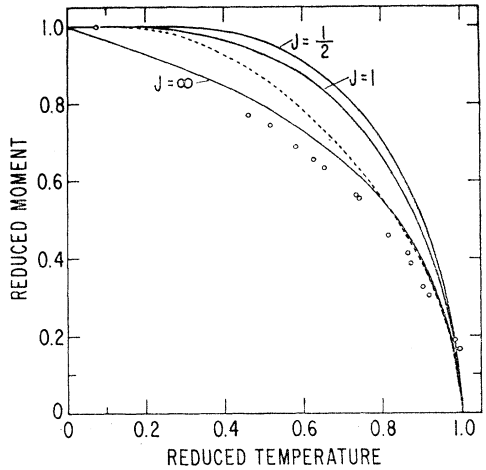

FIG. 7. Reduced moment versus reduced temperature for the iron-doped sample (2.25 at.% Fe), No. 11. The dashed line is reproduced from Fig. 4(a); it is a composite result. The solid lines are the molecular-field-theory predictions for angular momentum $J=\frac{1}{2}$, 1, and ∞.

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[15] M. B. Maple and H. L. Luo, Phys. Letters **25A**, 121 (1967). Alternatively, the enhanced resistivity may be caused by *s-d* scattering if the Fermi level lies in the *d* band.

[16] In addition to sample Nos. 4c and 5, each run in two directions, another sample (a single grain) was run in three mutually perpendicular directions, again showing little change in moment.

[17] H. L. Luo, L. Creveling, Jr., and J. P. Maita, Phys. Letters **25A**, 740 (1967).

which leads to an effective moment per Fe ion of about 3.8, corresponding to spin $\frac{3}{2}$. This is only approximate, but the value is reasonable.

4. *Kind of Ferromagnetism*

The question of what classification best fits the ferromagnetism of Au_4V is an interesting one. We state at the outset that we have no conclusive answer, but experimental evidence favors a model of localization in the molecular-field approximation. To begin with, consider C. It varies from sample to sample, much as it does in the case of the solid solutions (see Sec. 5 B 2), although the variation is less systematic. This may mean that only a fraction of the V ions possess localized moments, with the fraction varying from sample to sample. The maximum value of p is 1.76 [sample No. 5(1)]. This corresponds to spin $\frac{1}{2}$ if we assume all V ions are magnetic. This would normally imply $\mu(0)=1.0\mu_B$, but we are dealing here with a highly anisotropic ferromagnet in an imperfect crystalline state. These effects result in reduced values of the observed moment. The experimental values are 0.60 and $0.52\mu_B$ for measurements in perpendicular directions. Two other experimental results support this conclusion. Recently, Knapp and Chin[18] have succeeded in generating a sample closer to a single crystal in structure by annealing under stress; the moment is $0.84\mu_B$ per V ion. Cohen *et al.*[19] have made Mössbauer-effect measurements on ordered and disordered Au_4V and conclude that the moment is $0.92\mu_B$ per V ion.

Wohlfarth has pointed out[20] that the magnetic carrier ratio q_c/q_s,[21] for the first sample we reported,[12] is 1.91. Values for other samples are given in Table I, column 10. Claus *et al.*[22] have made magnetic measurements on Au_4V and give a value of 2.1 (their published value appears to be a misprint). These values are in fair agreement and fall much closer to the local moment value (1) than the itinerant value (>7), since T_c is 40–60°K. Moreover, the moments should be larger, as discussed above, resulting in still lower values of q_c/q_s.

Reduced moment offers further insight into the problem. We have already noticed the universal nature of $\mu(T)/\mu(0)$ versus T/T_c. At low T/T_c (<0.2) $\mu(T)/\mu(0)$ falls on the theoretical $J=\frac{1}{2}$ curve. As the temperature increases, it deviates and approaches $J=\infty$ (coinciding with it for $T/T_c>0.8$). A plot of $\mu(T)/\mu(0)$ and its square versus temperature for sample No. 5(1) is given in Fig. 8. It can be seen that the square is linear to 15 or 20°K below T_c, which agrees with a prediction of the molecular-field theory. (In fact, the agreement is better than it should be because the magnetization deviates from the $J=\infty$ curve at lower temperatures in a way that continues the linearity to lower temperatures.) This was found to be the case for all the samples measured. Moreover, the theory predicts that the product of the absolute value of the slope and T_c is equal to 3.00, 2.67, 2.45, 2.31, 2.21, and 1.67 for the cases spin $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, and the classical limit (spin→∞), respectively.[23] This quantity has been calculated and is the molecular-field parameter listed in Table I, column 11. The values scatter about 1.67 (spin→∞) in agreement with the $\mu(T)/\mu(0)$ versus T/T_c plots. For some reason, perhaps magnetocrystalline anisotropy, spin quantization does not manifest itself at temperatures close to T_c.

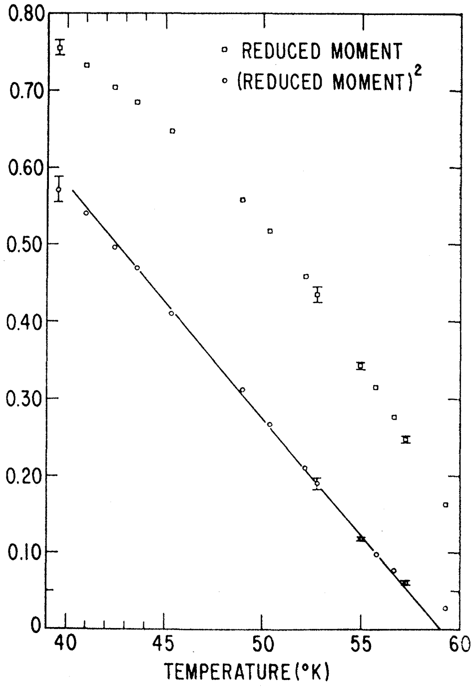

FIG. 8. Reduced moment and its square versus temperature for sample No. 5(1). The linearity in the square plot satisfies a prediction of the molecular-field theory.

Figure 9 is a plot of $\mu(T)/\mu(0)$ versus $(T/T_c)^{3/2}$ for sample No. 4c. There appears to be no linearity even at lowest temperatures. The absence of the usual spin-wave dependence may possibly be related to the combination of extreme anisotropy and crystal imperfection that exists in these samples. This contribution seems to be absent in the specific heat also.[17]

Finally, we note three additional experiments that have been done on Au_4V. Dunlap *et al.*[24] and Cohen *et al.*[19] have measured the hyperfine field of ^{197}Au by

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[18] G. S. Knapp (private communication).

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

[20] E. P. Wolhfarth (private communication).

[21] P. Rhodes and E. P. Wohlfarth, Proc. Roy. Soc. (London) **273**, 247 (1963).

[22] H. Claus, A. K. Sinha, and P. A. Beck, Phys. Letters **26A**, 38 (1967).

[23] In general,

$$|\text{slope}|\times T=\frac{5}{3}\frac{[(2S+1)^2-1]^2}{(2S)^2[(2S+1)^2+1]}.$$

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

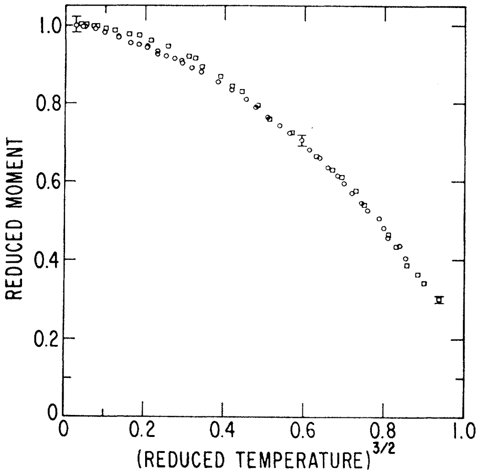

FIG. 9. Reduced moment versus (reduced temperature)$^{3/2}$ for sample No. 4c. The two symbols represent measurements made on the sample oriented in mutually perpendicular directions. Note the apparent absence of spin-wave reduction at low temperatures (little or no linearity in the reduced temperature range 0 to 0.5).

the Mössbauer technique and conclude that the moment is localized on V ions with little or no moment on Au ions. We[17] have measured the specific heat between 1.5 and 60°K with generally inconclusive results. The magnetic entropy appears to lie between $0.4R$ (R is the gas constant per mole) and $1.1R$; the discontinuity in the specific heat at T_c (ΔC_p) is insufficiently sharp to make any choice between a spin wave ($\Delta C_p = k$, Boltzmann's constant) or a spin-$\frac{1}{2}$ molecular-field ($\Delta C_p = 3/2k$) interpretation. However the unusually high density of states in ordered Au_4V (as determined by the electronic specific heat and χ_0) cannot be overlooked. In fact, the electronic specific heat of Au_4V is several times higher than that of the isotypic compounds Au_4Mn and Au_4Cr.[25] This comparison is significant because Au_4Cr is antiferromagnetic ($T_N \approx 400$°K)[26] and Au_4Mn is ferromagnetic ($T_c \approx 100$°K).[27] This may favor the itinerant model.

B. Disordered Alloys

1. *Introduction*

The main results are as follows:

(1) χ is field-independent for all accessible temperatures. There is a slight amount of nonlinearity in the magnetization-field diagrams for temperatures below about 2°K, but this can be accounted for by assuming the presence of magnetic impurities in amounts that agree with the spectrographic analyses. In fact, we used our magnetization data at 0.37°K to estimate the impurity level and then to correct the susceptibility data. The correction is appreciable (>1%) only below 20°K and is less than 10% of the measured value at 4.3°K (except for the splattered samples which had higher impurity levels).

(2) χ is temperature-dependent up to a concentration of 33 at.% V. The dependence can be described by a Curie-Weiss law, $\chi - \chi_0 = C/(T-\theta)$, with the appropriate choice of parameters.

(3) χ also depends on heat treatment. To describe this dependence we have selected three different heat treatments (described in Sec. 4) and subjected each sample to each in turn. Figures 10(a)–10(c) show χ versus T for samples of concentration 0.3, 5, and 20 and 30 at.% V, respectively. Figures 11(a)–11(c) show susceptibility difference $\chi - \chi_0$ and its reciprocal versus temperature difference $T-\theta$ for the same samples. These figures illustrate the Curie-Weiss nature of the temperature dependence and the effect of heat treatment on the Curie constant. (Data for the remainder of the samples are given in the Appendix.) Table II gives a complete summary of the experimental results. The Au sample was measured as-cast from the arc furnace, the V as-received from the supplier. Our value for V is larger than the listed one.[28] However, χ is sensitive with respect to sample preparation[29–31]; our value agrees with that of others[31] obtained from measurements on a similar sample.

Before proceeding, we would like to pause at this point and make clear the distinction between our experimental results (in the main summarized above) and our interpretation thereof (below). We have presented our results in terms of a Curie-Weiss description because it seemed to us the clearest, most concise way of doing so. No significance is attached to the description; in fact we give in the Appendix (Table IV) an alternative summary of the data. In our interpretation of the results, however, we do attach significance to their Curie-Weiss nature. Regardless of whether or not our interpretation is correct, the data (including their Curie-Weiss or any other description) remain valid.

2. *Curie Constant C*

Several observations can be made concerning the results summarized in Table II. When V is dissolved in Au in dilute amounts, some of the V ions appear to possess local moments (magnetic ions) while others do not. The concentration of magnetic ions increases with increasing concentration to a maximum at 5–10 at.% V and decreases thereafter until it vanishes completely at about 30 at.% V. Although the experimental accuracy

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[25] R. S. Toth, S. Shinozaki, A. Arrott, J. E. Noakes, S. A. Werner, and H. Sato, Bull. Am. Phys. Soc. **13**, 125 (1968).

[26] E. Wachtel and U. Vetter, Naturwiss. **48**, 156 (1961); E. Wachtel and U. Vetter, Z. Metallk. **52**, 525 (1961).

[27] A. Kussman and E. Raub, Z. Metallk. **47**, 9 (1956).

[28] "*Landolt-Börnstein,*" *Eigenschaften der Materie in Ihren Aggregat Zuständen, Part IX, Magnetic Properties I* (Springer-Verlag, Berlin, 1962), pp. 1–5.

[29] B. G. Childs, W. E. Gardner, and J. Penfold, Phil. Mag. **5**, 1267 (1960).

[30] D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, and D. E. MacLeod, Phys. Rev. **128**, 1550 (1962).

[31] D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, and D. W. Pracht, Phys. Rev. **135**, A455 (1964).

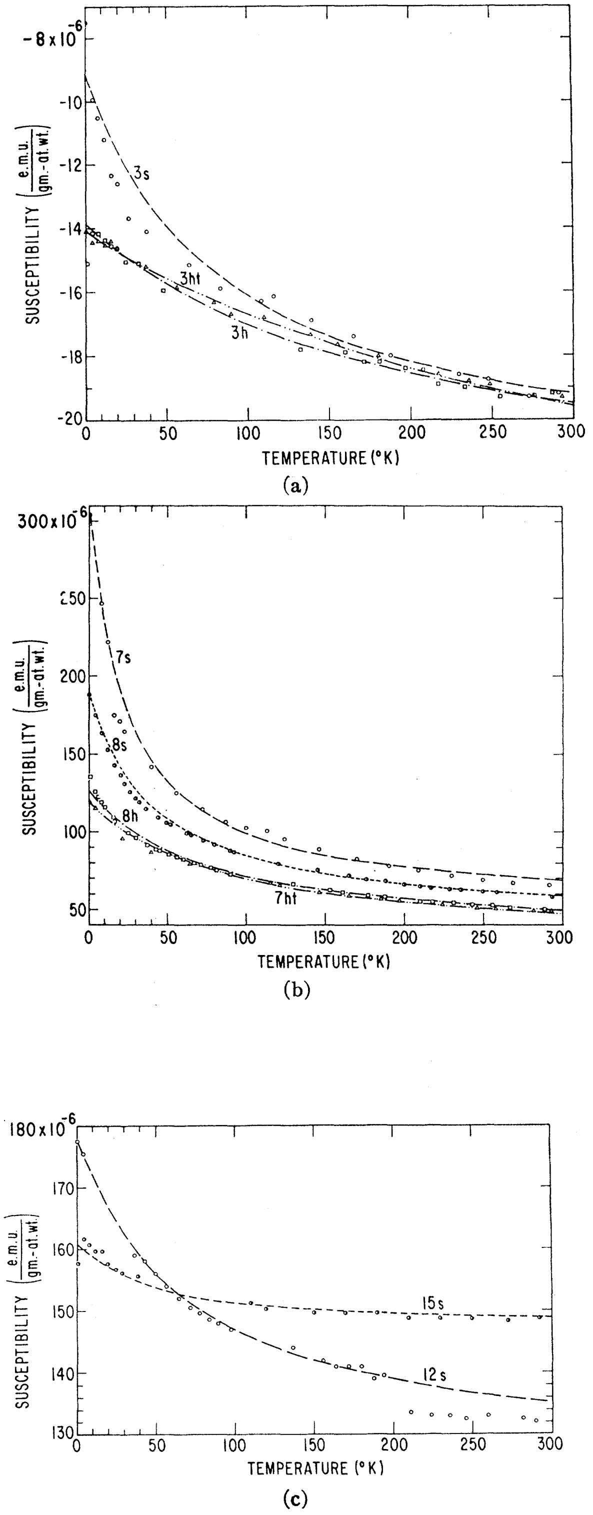

FIG. 10. Susceptibility versus temperature for (a) a dilute sample, No. 3 (0.3 at.% V), subjected to three different heat treatments; (b) two samples of intermediate concentration, No. 7 (5.00 at.% V) and No. 8 (5.02 at.% V), each subjected to two different heat treatments; (c) two concentrated samples, No. 12 (19.80 at.% V) and No. 15 (30.01 at.% V).

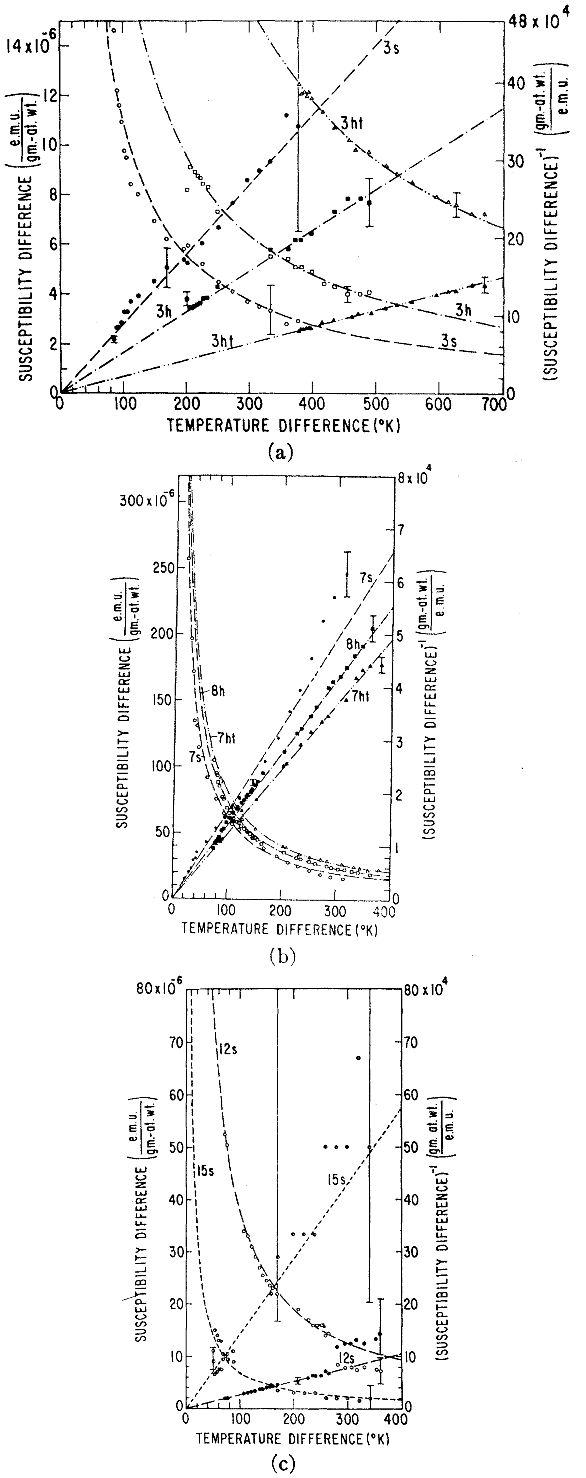

FIG. 11. (a), (b), and (c). Susceptibility difference $\chi-\chi_0$ (open and right-half-solid points) and its reciprocal (solid and left-half-solid points) versus temperature difference $T-\theta$ for samples No. 3, 7 and 8, and 12 and 15, respectively. These figures show the Curie-Weiss nature of the temperature-dependent component (and the accessible region of the reciprocal plot) and the effect of heat treatment on the Curie constant. The error bars are described in the text.

TABLE II. Data on solid solutions.

Sample[a]	Concentration α (at. % V)	Atomic weight	Average distance between vanadium ions (Å)	Magnetic impurity level[b] (ppm)	χ_0 [c] $\left(\frac{10^{-6}\text{ emu}}{\text{g at. wt}}\right)$	θ[d] (°K)	C[e] $\left(\frac{10^{-3}\text{ emu °K}}{\text{g at. wt}}\right)$	p[f] (μ_B)	Concentration of magnetic ions α_M[g] (at.% magnetic V)
Au	0	197.0			−27±0.5[k]				
1s	0.05	196.95	32.4	5	−27.2±1.0[k,l]				
1h				1.5	−26.5±0.2[k]	no temperature dependence			
1ht				1	−26.5±0.3[k]				
2s	0.10	196.85	25.7	5	−25.25[l]	−15	0.079	0.785	0.0043
2h				2	−25.25	−150	0.113	0.94	0.0061
2ht				0.5	−25.95	−246	0.650	2.25	0.035
3s	0.30	196.55	17.9	3.5	−22.1[l]	−86	1.114	1.70	0.060
3h				2	−23.3	−202	1.906	2.23	0.103
3ht				1.5	−26.5	−378	4.691	3.50	0.254
4s	0.50	196.25	15.0	3.5	−19.9[l]	−89	1.689	1.63	0.092
4h				1.5	−22.0	−248	3.239	2.25	0.175
4ht(2)[h]				1	−24.3	−304	5.107	2.82	0.276
4ht				1	−21.3	−178	2.521	1.98	0.136
5s	0.70	195.95	13.5	6	−16.1[l]	−80	2.736	1.75	0.148
5h				3	−17.4	−150	3.097	1.86	0.168
5ht				1.5	−20.7	−191	4.777	2.31	0.258
6s	1.00	195.55	11.9	6	−14.35[l]	−59	3.137	1.57	0.170
6h				3	−15.3	−121	3.805	1.73	0.206
6ht				2	−14.1	−137	4.151	1.80	0.224
7s	5.00	189.65	7.0	72	50.1[l]	−23	6.093	0.98	0.330
7ht[i]				5.5	26.75	−88	8.140	1.13	0.440
8s	5.02	189.65	7.0	31	40.0	−43	6.447	1.00	0.348
8h				6	30.7	−75	7.246	1.07	0.392
9s	9.91	182.5	5.5	46	83.1[l]	−28	6.057	0.69	0.328
9h				21	70.1	−84	7.393	0.76	0.400
9ht					ferromagnetic				
10s	14.92	175.2	4.8	23	107	−47	4.673	0.49	0.253
10h					103.2	−58	4.176	0.47	0.226
11s	15.00	175.1	4.8	13	110[l]	−31	3.981	0.46	0.216
11h				3.5	98.7	−76	5.335	0.53	0.288
12s	19.80	168.1	4.4	17	124.9	−72	3.797	0.39	0.206
12h					approximately 0.3% ferromagnetic				
13s	25.00	160.5	4.1	···	129.1	−33	1.445	0.21	0.078
14s	28.01	156.1	3.9	···	136.8[l]	−69	2.123	0.24	0.115
15s	30.01	153.1	3.8	···	146.7[l]	−50	0.700	0.14	0.038
16h	33.40	148.2	3.7	···	151±0.2[k]	no temperature dependence			
16ht[j]					ferromagnetic (Au_4V present)				
17h	37.00	142.95	3.6	···	152±5[k]	no temperature dependence			
18h	41.02	137.1	3.5	···	158±3[k]	no temperature dependence			
19h	45.06	131.2	3.4	···	171±2[k]	no temperature dependence			
20h	49.84	124.2	3.2	···	178±1[k]	no temperature dependence			
V		50.95		···	300±3[k]				

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[a] The suffixes s, h, and ht signify "splattered," "homogenized," and "heat-treated," respectively (see Sec. 4).

[b] As determined from the magnetization at 0.37°K (see Sec. 5 B 1).

[c] Temperature-independent component of the susceptibility χ.

[d] Critical temperature.

[e] Curie constant. $C \equiv (N_A p^2 \mu_B^2)/3k$, where N_A is Avogadro's number and k is Boltzmann's constant.

[f] Effective moment per vanadium ion as obtained from C.

[g] As obtained from $C = (\alpha_M N_A \mu_B^2 p^2)/3k$ assuming $p = 3.8$ (corresponding to V^{2+}). This corresponds to Vogt and Gerstenberg's α_M since they used the same value for p in their calculation.

[h] Heat treated for 1 week at 500°C.

[i] After homogenization, heat treated as follows: 14 days at 700°C, 14 days at 510°C, then 8 days at 350°C.

[j] After homogenization, heat treated as follows: 10 days at 700°C, then 3 days at 500°C.

[k] Uncertainty gives spread in experimental values for different temperatures.

[l] Corrected for Teflon container.

is poor at the lowest concentrations, it appears that the fraction of ions that are magnetic (the effective moment p is a measure of this) decreases below 0.3 at.% V and goes to zero with the concentration. Hence it appears that there is a lower, as well as an upper, limit to the concentration in which partial localization occurs. We shall discuss this further in Sec. 6 D below.

Turning now to the effect of heat treatment, we see that in practically every case increased heat treatment results in a larger C, or a larger fraction of magnetic ions. It is possible that this effect is caused by the formation of increasing amounts of Au_4V with increasing heat treatment, i.e., by clustering, but unlikely because of the nonzero fraction for the splattered samples. It is hard to imagine any clustering taking place in the splattering process. In addition one would expect very little ordering in the homogenized samples (indeed only about 0.3% ordering occurred in the 20 at.% V sample) since they were treated well above the ordering temperature, and considerably more in the heat-treated samples since they were treated at temperatures comparable to or a little above the ordering temperature. However, the increase in magnetic concentration with heat treatment is roughly uniform and relatively small for every concentration. Also ferromagnetism only occurs for concentrations above 5 at.% V in the heat-treated samples in agreement with the phase diagram as modified by Köster *et al.*[6] Finally, x-ray crystal-structure determinations failed to show the presence of any of the ordered phase in the nonferromagnetic samples. While all the above facts do not constitute conclusive proof, it nonetheless appears highly unlikely that Au_4V clusters exist in the dilute alloys.

Alternatively, if one looks at the effect of heat treatment on χ itself (see Appendix, Table IV) in order to check the possibility of nonmagnetic V clustering, the results are less clear cut. The susceptibility tends to decrease with increasing heat treatment, but there are several exceptions. Moreover one would expect this type of clustering to result in less temperature dependence (of which there is even less indication in the data) and perhaps a larger room-temperature χ because of the large Pauli paramagnetism of V (which is contradicted by the data).

3. *Critical Temperature θ*

The effect of heat treatment on θ (in fact, even the mere existence of θ) is very interesting. Kume[9] has accounted for θ in terms of the Kondo effect and we find no reason in this work to disagree. We do feel, however, that he has been overly restrictive in assuming that all the V ions are magnetic. This means that χ can no longer be described by a Curie-Weiss law (since now χ_0 must be approximately χ_{Au}). We feel that the possibility of the Curie-Weiss description for all concentrations and heat treatments is more than coincidental. Moreover, a varying magnetic concentration can explain the effect of heat treatment on θ. The effect is that increasing heat treatment results in a larger (in magnitude) θ for a given sample. Since the magnetic concentration increases, the nonmagnetic concentration must decrease. If we assume that increasing the ratio of the number of nonmagnetic V ions ($N_{\mathrm{nm\,V}}$) to the number of Au ions (N_{Au}) results in a progressive emptying of an initially full (when $N_{\mathrm{nm\,V}}/N_{\mathrm{Au}}=0$) d band, then a decrease in nonmagnetic concentration (hence a decrease in $N_{\mathrm{nm\,V}}/N_{\mathrm{Au}}$) with increasing heat treatment would raise the Fermi level closer to the top of the d band and hence decrease the density of states at the Fermi level. $|\theta|$ is given by

$$|\theta|\approx T_K\approx T_F\exp(-1/|I|\rho),$$

where T_K is the Kondo temperature, T_F is the Fermi temperature, I is the conduction-localized electron exchange parameter, and ρ is the density of states of one spin index per atom at the Fermi level.[32] Hence, this would result in a larger value of $|\theta|$ (assuming I is constant). Finally, we note that, for a given heat treatment, $|\theta|$ decreases with increasing concentration (hence increasing nonmagnetic concentration, since the magnetic concentration never increases faster than the total concentration) as expected from the above considerations.

It is tempting to try to draw further conclusions from θ, but such an attempt would very probably be unproductive because of the fact that, of all the quantities listed in Table II, it is the least accurate. An error of ±50°K would be none too large, implying that only broad trends in the data are meaningful. Before leaving θ, however, it is appropriate at this point to comment on the Kondo effect as an explanation for θ. At present it seems the only possible explanation for the phenomenon: a temperature-dependent χ describable by a Curie-Weiss law with negative θ but one which nonetheless has no discernible discontinuity at the corresponding temperature. Moreover it accounts for other, otherwise anomalous, behavior (resistivity, specific heat, etc.).[9,33] The Kondo effect can be handled theoretically only in the extreme dilution (i.e., no impurity-impurity interaction) limit, and even then only a crude indication that χ satisfies a Curie-Weiss law for temperatures well below the Kondo temperature is possible at present.[32] Nevertheless, the experimental results indicate that the predictions of the theory are applicable over a much wider range (in both concentration and temperature) than appears justifiable on the basis of the theory. χ satisfies a Curie-Weiss law up to the limit of temperature dependence (about 30 at.% V) and over the whole of the temperature range

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[32] For a complete discussion of the Kondo effect and list of related references, see M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. **40**, 380 (1968).

[33] K. Kume and T. Zempo, J. Phys. Soc. Japan **22**, 1115 (1967); K. Kume, *ibid.* **22**, 1116 (1967); J. O. Linde, Physica **24**, S109 (1958).

measured (0.37 to 900°K up to 15 at.% V, to 300°K for higher concentrations) including the region around T_K (about 300°K for concentrations less than ≈ 1 at.% V). The only experimental stipulation (at least if the Curie-Weiss dependence is to be preserved) is that the temperature dependence of the effective moment p be given by

$$p^2 = p_0{}^2 T/(T-\theta),$$

where p_0 is a constant. One reason the Kondo effect might persist to such high concentrations is that the magnetic concentration is in fact the significant one, not the total concentration, and it may be much smaller. The maximum value of the magnetic concentration (sample No. 7ht) is 0.44 at.% mag. V for $p=3.8$, or 2.13 at.% mag. V for $p=1.73$.

4. *Temperature-Independent Component of the Susceptibility* χ_0

The behavior of χ_0 is in accord with the conclusions above. Increased heat treatment almost always results in a decreased χ_0. χ_0 consists of the core diamagnetism and the conduction spin paramagnetism. Since heat treatment increases the magnetic fraction, the nonmagnetic fraction must decrease. This results in a (relatively very large) decrease in the paramagnetic contribution and a (relatively much smaller) increase in the diamagnetic contribution, both of which decrease χ_0. In this regard, notice that for the 0.3 at.% V heat-treated sample (No. 3ht), where the nonmagnetic fraction is close to zero, χ_0 approaches the value for Au.

Assuming, again, a simple emptying of the (initially full) *d* band with increasing nonmagnetic ion concentration, one would expect χ_0 to increase (at least initially), which is indeed the case (Fig. 12). (It appears that χ_0 is linear over two regions, 0 to 10 and 10 to 50 at.% V). It is interesting (but perhaps purely coincidental) that the high concentration extrapolation is close to the room-temperature value of χ for the intermetallic compound AuV_3 [34] and terminates in the midst of the various published values for $V[(270\text{–}300)\times 10^{-6}\,\text{emu}/(\text{g at. wt})]$.

The slope of χ_0 versus concentration for low concentrations varies with heat treatment but is large in each case. In the limit of the free-electron model, the slopes lead to incremental density-of-states values of 0.70, 0.53, and 0.43 per eV per atom per at.% V for the splattered, homogenized, and heat-treated samples, respectively; on the other hand, if we assume no Landau diamagnetic contribution (typical for transition elements), the slopes lead to values of 0.47, 0.35, and 0.29, respectively. The value from specific-heat data is 0.26 [35]; it seems to agree with the prediction of the Kondo theory as pointed out by Kume.[9] There may be a discrepancy between the susceptibility and specific-heat values although it is difficult to be certain in view of the variation caused by heat treatment (in this regard homogenization most closely approximates the heat treatment of the specific-heat samples). It would be interesting to see what effect heat treatment has on specific heat and whether the change in the slope of χ_0 versus concentration at 10 at.% V is reflected in the specific heat.

We have thus far assumed (and will continue to do so in the remainder of the paper) that the Au matrix plays a strictly passive role, simply participating in the formation of the crystal structure. The rapid increase in χ_0 at low concentrations, however, led us to wonder if perhaps the Au might contribute to it, at least. We assumed that Au ions with one or more V nearest neighbors (only these would "feel" the presence of the V because of screening) developed an enhanced susceptibility, $\chi_{m\text{Au}}$, while those without did not. The probability of a site having no V nearest neighbors is $(1-\alpha)^{12}$ (assuming random distribution), where α is

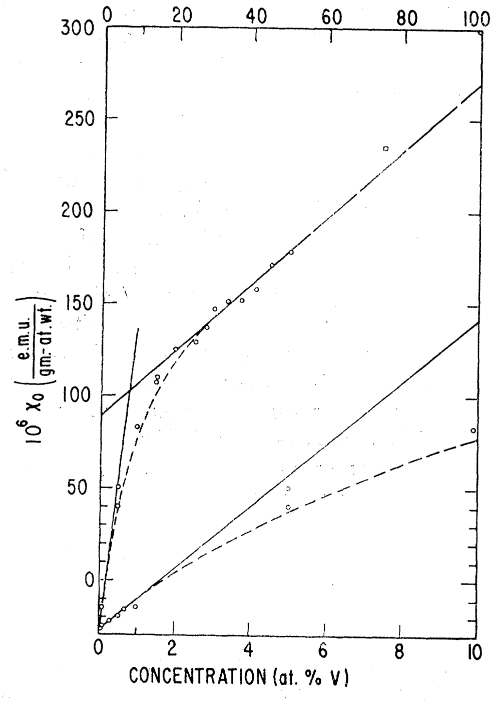

FIG. 12. The temperature-independent component of the susceptibility of splattered (concentration, α, <33 at.% V) and homogenized ($\alpha > 33$ at.% V) samples versus concentration. The function $\chi_0 = [89 + 181\alpha - 116(1-\alpha)^{13}]\times 10^{-6}$ emu/(g at. wt) is plotted as the dashed curve (see Sec. 5 B 4). The lower curves are plotted according to the lower scale, the upper curves according to the upper scale. The square point is the room-temperature value of the susceptibility of the intermetallic compound AuV_3 (see Ref. 34).

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[34] From the results of H. J. Williams and R. C. Sherwood, Bull. Am. Phys. Soc. **5**, 430 (1960), given in A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).

[35] F. J. DuChatenier, J. DeNobel, and B. M. Boerstoel, Physica **32**, 561 (1966). We have neglected their 1.4 at.% V point in arriving at our value.

the V concentration. Hence χ_0 is given by

$$\chi_0=\alpha\chi_{\mathrm{V}}+(1-\alpha)[1-(1-\alpha)^{12}]\chi_{m\mathrm{Au}}+(1-\alpha)(1-\alpha)^{12}\chi_{\mathrm{Au}},$$

where $\chi_{\mathrm{V}}=270\times10^{-6}$, $\chi_{\mathrm{Au}}=-27\times10^{-6}$, and $\chi_{m\mathrm{Au}}=89\times10^{-6}$ emu/(g at. wt) (the latter was obtained by extrapolating the high-concentration data, where $(1-\alpha)^{12}$ is negligible, to zero). Therefore,

$$\chi_0=[89+181\alpha-116(1-\alpha)^{13}]\times10^{-6}\ \text{emu/(g at. wt)}.$$

This function is plotted as the dashed curve in Fig. 12; the intermediate-concentration data fall remarkably close. Thus it seems the Au might well participate in the large apparent increase in the density of states with increasing concentration at low concentrations. It is tempting to attribute this to some sort of band deformation caused by a nearest-neighbor Au–V interaction resulting in the Fermi level occurring in the *d* band, so as to take advantage of the much greater density of states occurring there. This would account for the rapid increase in electronic specific heat also, of course, and perhaps even the rapid increase in resistivity[6,33] since the *s-d* scattering mechanism would now be operative.[36]

5. *Other Results*

Before concluding this section we shall discuss a few further results. Sample Nos. 12, 13, 14, and 15 (20–30 at.% V) were splattered in order to avoid the formation of any ordered phase. We found that it was unnecessary to do this for the samples of higher concentration. The process of homogenization is sufficient to suppress the ordering completely. We annealed sample No. 16 (33.40 at.% V) and found that it was ferromagnetic. X-ray analysis indicated the presence of $\mathrm{Au_4V}$. The phase diagram shows the presence of another ordered phase, $\mathrm{Au_2V}$, in this region; our results suggest that the situation may be more complicated.

There exists a peak in χ for homogenized samples at low temperatures (<13°K), in the concentration range 0.1 to 10 at.% V [see Figs. 10(a), 11(a), 15(a), and 15(e)]. The peak is very small (the susceptibility difference between the peak value and the value at 0.37°K is always less than 2.2×10^{-6} except sample No. 9h, for which it is 5.5×10^{-6}) and is close to the limit of experimental accuracy. It may correspond to the peaks reported by Lutes and Schmit[8] for dilute alloys of Cr, Mn, and Fe in Au, although in this case no remanence appeared below the temperature at which the peak occurred.

6. *Comparison of Data*

Finally, a few words should be said about our results as compared with the earlier work (Fig. 2). In view of the fact that heat treatment influences χ, we do not find the deviations, one set of results to another, excessive (with the exception of Lutes and Schmit's result). The curves representing our results in Fig. 2 are from our homogenized samples, since this heat treatment most closely approximates those used in the other investigations. Nonetheless, variations in heat treatment do remain.[37] Vogt and Gerstenberg's values for χ_0 agree with ours. Their values for C and θ are generally somewhat larger; this is probably due to the fact that they did not have the most temperature-dependent region (0 to 90°K) accessible to them. Lutes and Schmit's anomalously high values may result from the presence of a large amount of magnetic impurities (for which no correction appears to have been made) since their measurement was made only over a temperature interval in which impurities are significant.

6. STATISTICAL MODEL

A. General Considerations

We have seen that the magnetic properties of disordered Au–V alloys can be interpreted in terms of a partial spin localization among the V ions. The concentration of these "magnetic" ions depends on the total concentration; increasing from zero, reaching a maximum, then decreasing to zero at about 30 at.% V. The physical reality of this magnetic fraction receives dramatic confirmation in the ferromagnetic ordered compound $\mathrm{Au_4V}$; the fraction suddenly increases to 1 and many of the manifestations of local moment, molecular-field-approximation ferromagnetism are observed.

It is possible to account semiquantitatively for this behavior by assuming that, for V dissolved in Au, there exists a critical nearest V neighbor distance. If a V ion has a nearest V neighbor within this distance, it has no local moment. But if not, then it does have a local moment. There is ample precedent for such behavior,[38] and Vogt and Gerstenberg[7] discuss the possibility specifically for V in Au. Claus *et al.*[22] have made essentially the same assumption in describing their results on $\mathrm{Au_4V}$ and substitutional alloys involving Nb and Ta. They can account for their results by assuming that nearest V ion pairs at distances equivalent to the nearest neighbor distance in the Au lattice do not have local moments, but that pairs at distances equivalent to the

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[36] In this regard, note the rather striking similarity between Koster *et al.*'s resistivity as a function of concentration (Fig. 1, p. 683, Ref. 6) and our Fig. 12.

[37] Vogt and Gerstenberg's samples were repeatedly heat treated at 1000°C for 1 h, then quenched in water until no further change in the room-temperature susceptibility occurred. Lutes and Schmit's sample was heat treated at 1000°C for 6 h, then quenched in water. Kume's samples were alloyed in a beam furnace with several meltings, then allowed to cool to room temperature with no further heat treatment. He heat-treated one sample (1.0 at.%) at 800°C for 10 days and reported no material change in the susceptibility.

[38] See, for example, J. B. Goodenough, *Magnetism and the Chemical Bond* (John Wiley & Sons, Inc., New York, 1963), for a discussion (in particular the summary on p. 26 ff) and references.

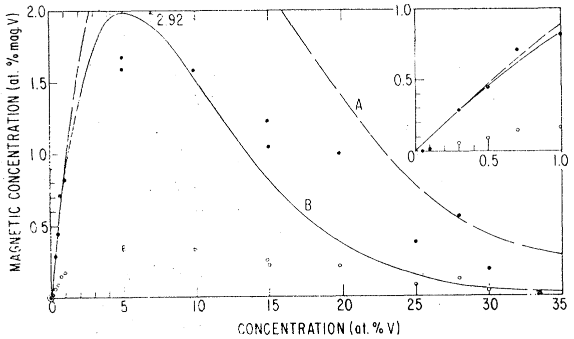

FIG. 13. Magnetic concentration versus concentration. The inset is on an expanded horizontal scale to show low-concentration data. The solid points were computed from the Curie constants assuming $p=1.73$, the open points assuming $p=3.8$ (see Table II, Ref. g). The curves A and B are statistical estimates of the magnetic concentration; they are plots of the functions $\alpha(1-\alpha)^{12}$ and $\alpha(1-\alpha)^{18}$, respectively, where α is the concentration (see Sec. 6 B in the text). The maximum value of $\alpha(1-\alpha)^{12}$ (curve A) is ≈ 2.92 and occurs at $\alpha \approx 0.07$ (the arrow).

second and third nearest neighbor distance do have local moments.[39]

B. Statistical Determination of the Concentration of Magnetic V Ions, α_M

It is now necessary to look at the crystal lattice spacings. They are given in Table III. Only the V sites are considered in the Au_4V crystal structure; we assume the Au serves only to help generate the structure, not participate in the magnetic behavior (except possibly contribute to χ_0 as discussed in Sec. 5 B 4). Since for concentrations exceeding about 30 at.% V spin localization disappears, we must assume that the critical distance is greater than the first nearest neighbor distance, 2.86 Å.[40] On the other hand, localization in ordered Au_4V indicates that the critical distance is less than 4.95 Å, perhaps less than 4.0 Å.

TABLE III. Neighbor parameters for Au and Au_4V lattices.

Neighbor	Au Number	Au Distance (Å)	Au_4V (vanadium sites only) Number	Au_4V (vanadium sites only) Distance (Å)
1st	12	2.85	2	4.0
2nd	6	4.05	8	4.95
3rd	24	4.95	4	6.4
4th	12	5.75	8	6.5

In order to make a comparison with experiment, we have calculated the probability that a given lattice site has no V ion as a (A) nearest, and (B) nearest or next nearest neighbor, assuming a random distribution. The probability is then given by $(1-\alpha)^n$, where n is the number of lattice sites excluded (12 for case A, 18 for case B) and α is the concentration. Then the magnetic concentration α_M is the product of this and α. These are plotted as curves A and B in Fig. 13. Our splattered sample data most closely satisfy the random distribution requirement, so that magnetic-concentration data is plotted. In addition, we have recomputed α_M assuming $p=1.73$ and plotted these results also.

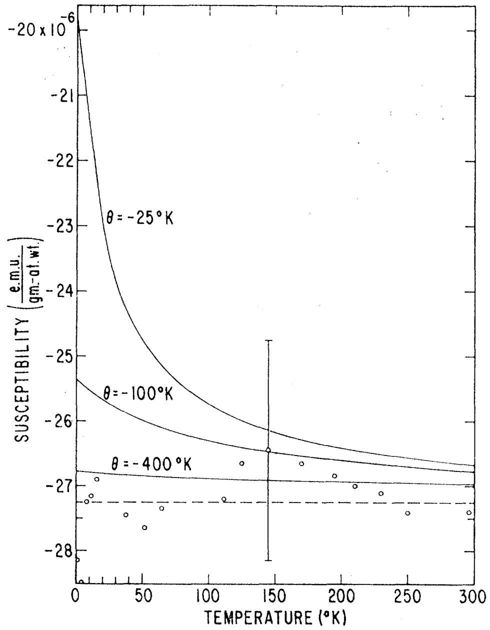

FIG. 14. Susceptibility versus temperature for sample No. 1s (0.05 at.% V) showing the apparent lack of localization at that concentration. The solid lines are Curie-Weiss plots assuming $\alpha_M=0.0005$ and $p=1.73$ for the three critical temperatures indicated. The dashed line is the temperature-independent part of the susceptibility.

C. Discussion of Results

There is fair agreement between curve B and the experimental data corresponding to $p=1.73$, although it certainly is not exact. There are several possible reasons for the deviations. The effective moment may depend on the magnitude of the spacing, or on the number of neighbors of a certain order (as suggested by Claus *et al.*[22]); we have assumed implicitly that it is fixed. Spin localization may not even occur until there are a certain minimum number of neighbors; perhaps a

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[39] As an interesting sidelight, we note that their result on the disordered alloy 20 at.% V is in conflict with ours; they observe no temperature dependence whereas we do [Table II and Figs. 10(c) and 11(c), sample No. 12s]. This is presumably because of the sensitivity of their apparatus. Actually, their sample corresponds to our sample No. 12h in heat treatment, rather than No. 12s, and No. 12h has considerably more temperature dependence, since about 0.3% of it is ferromagnetic; this is the sample with which we discovered the ferromagnetism of Au_4V.

[40] It is interesting that for concentrations above 30 at.% V even the impurity nonlinearity in the magnetization at 0.37°K disappears, indicating that not only V but also Fe (the main magnetic impurity) spin localization is destroyed.

certain spatial configuration of critical neighbors is required.[38]

Curve B represents α_M assuming none of the first or second nearest neighbors are V ions. Ordered Au_4V has two nearest neighbors at a distance close to the second nearest neighbor distance in the Au lattice, so the restriction of no second nearest neighbors may be too severe. As a further indication of this, the experimental magnetic concentration is between the theoretical curves in the higher concentration region where this choice is important. An effective moment of 1.73 agrees with the ordered Au_4V values, but is difficult to reconcile with some of the homogenized and heat-treated sample values. Effective moments greater than 1.73 occur, however, only in samples of concentration less than 1 at.% V. Here the experimental accuracy is least good and, moreover, there are large negative values of θ making the determination of C subject to further uncertainty. Alternatively, V may experience spin localization corresponding to spin $\frac{3}{2}$ or more in very dilute concentrations with this value decreasing as nearest V neighbor distances decrease.

D. Anomalous Decrease in α_M

One further point with regard to Fig. 13 requires comment. The insert in particular shows that, while agreement with the theoretical curves is in general very good in the very dilute range, nonetheless there is a deviation below 0.3 at.% V. Here the experimental values of α_M appear to drop off to zero. The above remarks concerning experimental accuracy in this concentration range again apply, except that, for splattered samples, θ is much smaller in magnitude (see Table II, column 7) making the determination of α_M more accurate. This is illustrated graphically in Fig. 14 where the susceptibility of Sample No. 1s versus temperature is plotted along with the function

$$\chi=[-27.25+188/(T-\theta)]\times10^{-6}$$

for three values of θ: -25, -100, and -400°K. The Curie constant is determined assuming $\alpha_m=\alpha=0.0005$ and $p=1.73$, a value typical for splattered samples in the concentration range 0 to 1 at.% V. From the figure it can be seen that it is possible that the deviation is due to experimental error, but rather more likely that it is not (especially since $\theta\approx-50\pm25$°K for this concentration). Narath *et al.*[41] have done nuclear magnetic resonance work on Au–V alloys in the concentration range 0.1 to 10 at.% V and find no anomalous behavior in the dilute region. However, there may be no contradiction because their heat treatment corresponds to our homogenization process, and for the 0.1 at.% V sample (No. 2h) α_M is closer to α. Further work is required to determine whether or not the two techniques yield compatible results.

TABLE IV. Susceptibility at certain temperatures.

Sample	Concentration α (at. % V)	Susceptibility [10^{-6} emu/(g at. wt)] 0°K	100°K	200°K	300°K
Au		-27 ± 0.5[a]			
1s	0.05	-27.2 ± 1.0[a]			
1h		-26.5 ± 0.2[a]			
1ht		-26.5 ± 0.3[a]			
2s	0.10	−23.5	−25.0	−25.0	−25.0
2h		−24.3	−24.8	−24.95	−25.0
2ht		−23.3	−24.0	−24.5	−24.75
3s	0.30	−9.1	−16.1	−18.2	−19.3
3h		−13.9	−16.9	−18.6	−20.0
3ht		−14.1	−16.7	−18.4	−19.5
4s	0.50	−1.0	−10.9	−14.0	−16.1
4h		−8.9	−12.7	−14.75	−16.1
4ht		−7.1	−12.2	−14.6	−15.8
4ht(2)		−7.5	−11.8	−14.1	−15.8
5s	0.70	20.6	−0.4	−6.4	−9.4
5h		3.0	−5.0	−8.5	−10.6
5ht		4.3	−4.4	−8.5	−10.8
6s	1.00	38.9	5.4	−1.6	−5.6
6h		16.0	1.8	−3.4	−6.3
6ht		16.0	3.4	−1.8	−4.0
7s	5.00	310	103	77	65
7ht		120	70	55	49
8s	5.02	189	85	66	57
8h		137	72	57	50
9s	9.91	298	134	110	100
9h		160	110	96	88
10s	14.92	206	139	126	120
10h		175	130	119	115
11s	15.00	239	143	127	120
11h		170	129	118	114
12s	19.80	177	147	138	130
13s	25.00	173	140	134	130
14s	28.01	170	149	145	143
15s	30.01	161	151	149	149

[a] Temperature-independent; uncertainty gives spread in experimental values for different temperatures.

As to what might cause this effect, if it exists at all, we can only conjecture. One possibility is that there exists an upper, as well as a lower, limit on V–V nearest neighbor spacing for spin localization to occur. This would result in a quadratic dependence of α_M on α for very low α. It is impossible to say what the dependence is below 0.3 at.% V, but it certainly appears to be linear above that value of α. This implies (on carrying out the appropriate statistical calculation) that the upper limit would have to be greater than 12 Å. We have no idea why such an upper limit should exist.

Another possibility relates to the rigid-band interpretation of χ_0 (Sec. 5 B 4). If the Fermi level lies just

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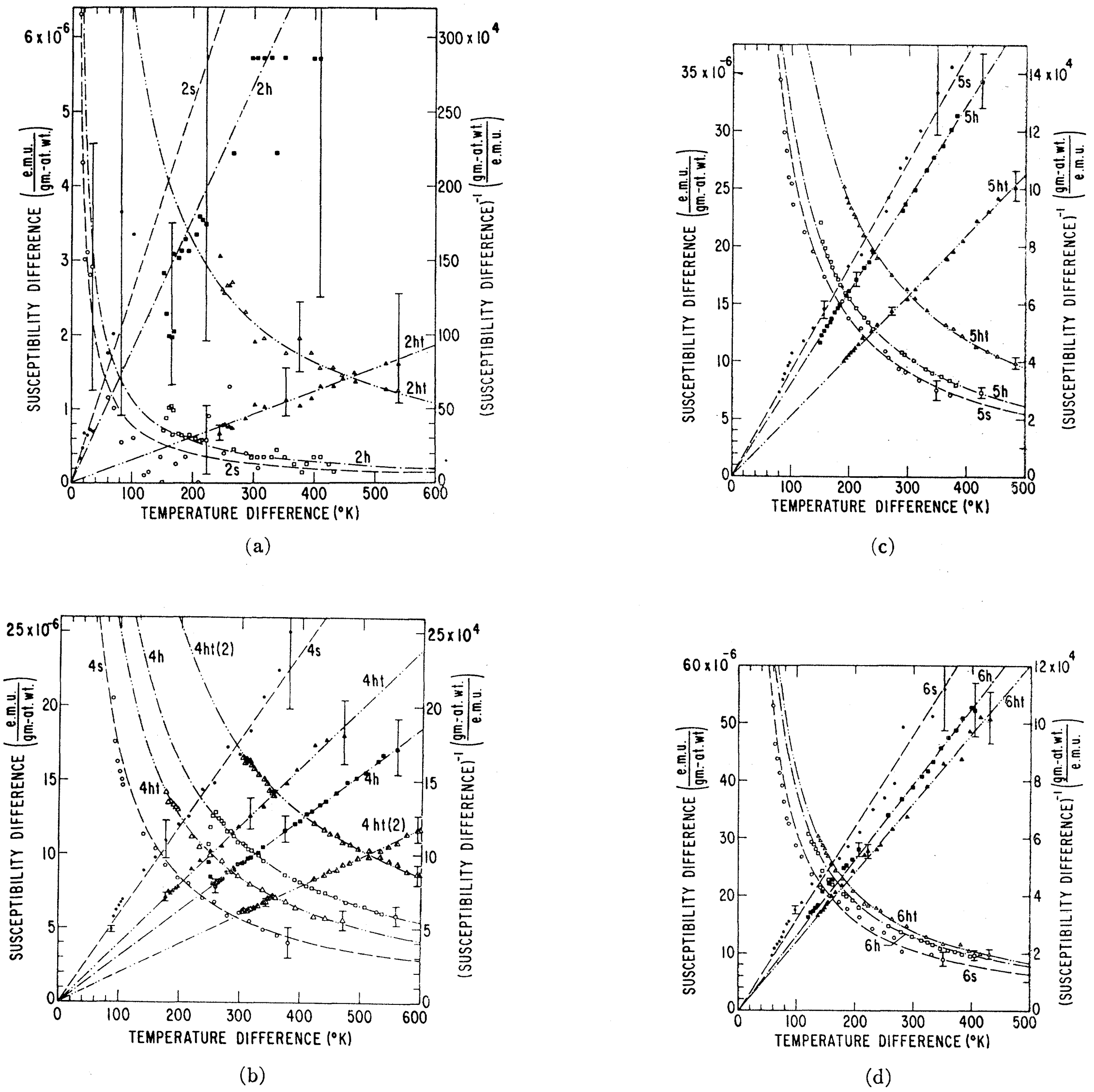
[41] A. Narath, A. C. Gossard, and J. H. Wernick, Phys. Rev. Letters **20**, 795 (1968).

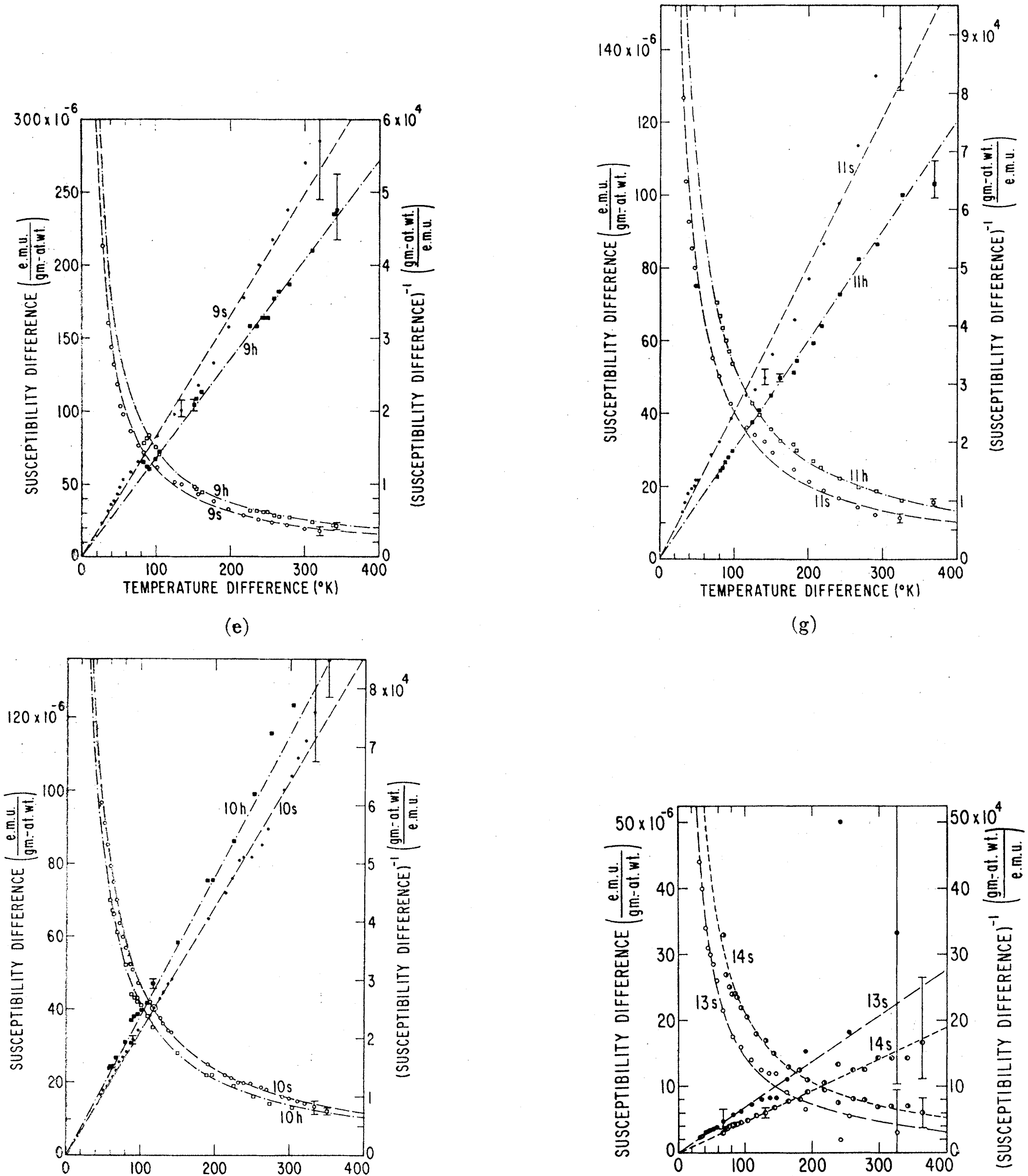


(a) (c) (b) (d)

FIG. 15. Susceptibility difference $\chi-\chi_0$ (open and right-half-solid points) and its reciprocal (solid and left-half-solid points) versus temperature difference $T-\theta$ for samples (a) No. 2 (0.1 at.% V), (b) No. 4 (0.5 at.% V), (c) No. 5 (0.7 at.% V), (d) No. 6 (1.00 at.% V), (e) No. 9 (9.91 at.% V), (f) No. 10 (14.92 at.% V), (g) No. 11 (15. 0 at.% V), and (h) No. 13 (25.00 at.% V) and No. 14 (28.01 at.% V).

above the top of the *d* band in Au, then the initial addition of vanadium would result in lowering the Fermi level through the *s* band before it reaches the top of the *d* band. Only when the Fermi level reaches the *d* band might localization begin to occur. This would result in a lower limit in α, below which α_M is zero. It would also mean that χ_0 is virtually constant over this concentration interval. There is a hint of this in the data, the 0.05 at.% V χ_0 value falls within the range of χ_{Au}, but the "evidence" is far from conclusive.

Finally we note that heat treatment increases α_M, indicating that magnetic spacing is favorable energetically. Heat treatment evidently makes possible some ionic migration resulting in an increased α_M. Migration would not affect α_M in very dilute concentrations, however, because the existence of a lower spacing limit is irrelevant in this case. But it is in these concentrations that the biggest percentage changes take place. This provides further support for the existence of an upper spacing limit. Heat treatment could then be thought of as causing primarily "clustering" (in this special sense) in very dilute samples and "declustering" in concentrated samples, with the two processes occurring simultaneously and to varying extents in intermediate



(e) (g)

(f) (h)

FIG. 15. (*Continued.*)

concentrations.[42] The possibility of a nonmagnetic V clustering has already been discussed (Sec. 5 B 2).

7. CONCLUDING REMARKS

We have seen that the magnetic properties of Au–V alloys can be described as follows: When V is dissolved in Au in dilute amounts (<33 at.% V) a fraction of the V ions acquire localized moments having effective moments in the range 0 to 3.8. This fraction depends on concentration in a way that can be semiquantitatively described in terms of a V–V nearest neighbor critical distance range. The range (approximately 4 to 12 Å) appears to have an upper as well as a lower limit

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[42] The discussion of $|\theta|$ in Sec 5 B 3 is not invalidated by subsequent results but must be modified. If we assume that the Au matrix contributes to χ_0 as discussed in Sec. 5 B 4, then the density of states at the Fermi level depends on $(N_{\text{nm V}}+N_{\text{nn Au}})/N_{\text{Au}}$ instead of $N_{\text{nm V}}/N_{\text{Au}}$ ($N_{\text{nn Au}}$ is the number of Au ions having at least one V nearest neighbor). $N_{\text{nn Au}}$ is probably insensitive to heat treatment, however, because (1) the degree of migration envisaged here is small since changes in α_M are small and (2) increases in $N_{\text{nn Au}}$ on "declustering" would be canceled by decreases resulting from "clustering." Hence $N_{\text{nn Au}}/N_{\text{Au}} \approx$ constant and can be ignored in the subsequent discussion on $|\theta|$.

(i.e., the magnetic fraction disappears for concentrations less than about 0.3 at.% V). V ions must have one or more nearest neighbors within this range in order to have a localized moment. This applies to random solutions; an ordered structure with the V–V nearest neighbor distance in the critical range should have all V ions magnetic. This is, in fact, the case with Au_4V (if the spin value is $\frac{1}{2}$), where there are two nearest neighbors at a distance of 4.0 Å. Moreover there is an exchange mechanism present since the compound is ferromagnetic with a T_c of about 60°K.

Might there not exist other such magnetic systems (composed of nonmagnetic metals) as yet undiscovered? After all, there is no reason why Au mixed with V should be unique in this regard. It is true that V lies on the fringe of the Fe series, but so does Co (Kume[9] has suggested that it might behave in Au like V, and Lutes and Schmit's[8] Au–Co sample suggests that it indeed does) and, by a slight stretch of the imagination, the second-row transition elements around Fe (Mo to Pd).

What requirements are there for a system to behave like Au–V and what criteria might be derived from the results on this system? Localization must, of course, take place. The Fe series elements are the most favorable followed by the elements mentioned above. Ti offers a counterexample; Vogt and Gerstenberg[7] have shown that no localization takes place in the dilute alloys and that there is no anomalous increase in χ_0 (equal to χ in this case). We have measured Au_4Ti and found no temperature dependence. For Au–V a critical V–V nearest neighbor range exists, and this may be the case for other possible ions, especially those not in the Fe series.

The matrix must be magnetically inert; for most solute ions it would probably have to have no *d* band or one that is filled. We have measured χ for samples containing 1 at.% V in Pt and Pd and found no temperature dependence different from that of the matrix. We have also measured χ for the compounds Pt_2V, Pt_3V, Pd_2V, Pd_3V, Ir_3V, and Rh_3V at low temperatures (0.37–4.3°K) and in no case is there any indication of localization or ordering. This might result from the proximity of the nearest neighbors, especially in the case of Pt_2V and Pd_2V. (The V ions in Pd_3V have four V nearest neighbors at a distance of 3.85 Å, and those in Pt_2V and Pd_2V, two at 2.75 Å.) But we feel it is more likely due to the incompletely filled *d* band of the host. Hence, the best matrices (unsurprisingly) are probably Cu, Ag, and Au, but others such as Zn, Cd, Hg, and the elements with unfilled *s* and *p* bands are possibilities.

Finally, for magnetic ordering, an exchange mechanism is required (and an ordered structure, of course). We do not know what provides this in Au_4V, but the intervanadium spacing seems too great for direct exchange to play a role. The large density-of-states value might be critical in this regard; perhaps there is a *d*-conduction–*d*-localized-electron exchange interaction. This would require that the matrix have one or more (filled) *d* bands.

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APPENDIX

The remainder of the data on the disordered samples is given in Fig. 15 in the form $(\chi-\chi_0)$ and $(\chi-\chi_0)^{-1}$ versus $T-\theta$ (see Sec. 5 B 1). An alternative description of the experimental results is presented in Table IV, where the values of χ at 0, 100, 200, and 300°K are given for those samples having temperature-dependent χ's.