III. CONCLUSIONS

It has been possible to interpret the sublattice magnetizations in EuIG by means of the spin-wave theory and the molecular-field approximation. Below approximately 30°K the $T^{3/2}$ term of the acoustical spin-wave mode appears to predominate, allowing a determination of the dispersion constant D. This determination, however, makes use of the effective g value and the anisotropy field. The value of these quantities as obtained from ferromagnetic resonance may not be applicable to the thermal spin waves having energies comparable to k_BT above 4°K. This consideration may explain the discrepancy with the D obtained from microwave instabilities.[7] The c sublattice magnetization was found to be accurately described by the theory of Wolf and Van Vleck[1] provided that only the d sublattice contributes to the exchange field at the c sites. This supports the evidence from previous experiments that the c-a interaction is much weaker than the c-d interaction.

Note added in proof. Atzmony *et al.*[10] have recently reported measurements of the hyperfine field acting on Eu^{153} nuclei in various rare-earth iron garnets. By comparing the fields in YIG and LuIG with those in other garnets, they deduced values for the c-c exchange interaction in the latter. For EuIG at 4.2°K, they estimated that the exchange field at a c-site is reduced by $(3\pm1)\%$ by the presence of the Eu^{+3} neighbors. If this contribution to H_{ex} is included in the molecular-field analysis of our paper, a good fit to experiment is obtained for $J_{cd}=-2.73$ cm^{-1}, $J_{cd}'=-0.23$ cm^{-1}, and $J_{ca}=0$. The only significant change from our previous analysis is the increase of J_{cd}' by 25%.

ACKNOWLEDGMENTS

The authors are indebted to Dr. A. B. Harris for several helpful conversations, and to Dr. J. H. Van Vleck and Dr. N. L. Huang for their comments on the results.

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PHYSICAL REVIEW VOLUME 170, NUMBER 2 10 JUNE 1968

Pressure Dependence of the Magnetic Transitions in Fe-Rh Alloys*

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(Received 18 September 1967; revised manuscript received 28 December 1967)

The pressure coefficients of the Curie temperature θ and the first-order transition temperature T_0 have been measured for two binary and three ternary alloys containing Fe and Rh. The coefficients are constant with pressure for all the alloys up to 25 kbars. The existence of a triple point in the P-T plane is demonstrated for these alloys. At pressures above the critical pressure, there is no ferromagnetic state, only antiferromagnetic and paramagnetic, consistent with Hargitai's theory that Rh atoms have no moment in the antiferromagnetic state. The pressure data and Kouvel's field-dependence data are used for comparison with the ratio of volume change to magnetization change as predicted from thermodynamics. Exchange inversion is discussed and ruled out as an acceptable model for the magnetic behavior. The effects of heat treatment on T_0 and dT_0/dP and the relationship between T_0 and dT_0/dP are also discussed.

I. INTRODUCTION

In recent years a great deal of work has been done on the magnetic properties of the Fe-Rh alloys (50–65 at.% Rh) which exhibit a first-order transformation from the antiferromagnetic (AFM) state to the ferromagnetic (FM) state with increasing temperature. Magnetization,[1–9] magnetostriction,[3,10] crystallographic,[1–3,6,9,11–14] Mössbauer,[15,16] and neutron diffraction[15–19] measurements have been performed at atmospheric pressure. High-pressure studies[3,4,7,20] have also been performed by several investigators in order to obtain the pressure coefficient of the first-order transition

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

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TABLE I. Summary of the first-order transition temperatures, the Curie temperatures, and their pressure coefficients for the alloys investigated.

Composition[a]	T_0 (°K)	θ (°K)	(dT_0/dP) (°K/kbar)	$(d\theta/dP)$ (°K/kbar)
$Fe_{0.490}Rh_{0.510}$	316	667	5.75	−0.60
$Fe_{0.472}Rh_{0.528}$	315	661	5.40	−0.75
$Fe_{0.483}Rh_{0.477}Ir_{0.040}$	528	644	2.45	−1.20
$Fe_{0.483}Rh_{0.459}Ir_{0.058}$	570	624	~2.2	−1.0 to −1.4
$Fe_{0.477}Rh_{0.507}Pd_{0.016}$	272	661	6.55	−0.90
$Fe_{0.50}Rh_{0.50}$[b]	353	660	4.33	...
$Fe_{0.48}Rh_{0.52}$[c]	333	675[d]	6.3	...
$Fe_{0.47}Rh_{0.53}$[e]	335	...	5.1	...
$Fe_{0.50}Rh_{0.50}$[f]	370[d]	680[d]	4.7	−0.60

[a] Compositions with no superscript are from this work; water quenched from 1300°K.
[b] Reference 3.
[c] Reference 4.
[d] Approximate values.
[e] Reference 7.
[f] Reference 20.

temperature T_0 and of the Curie temperature θ. In this paper we present values of (dT_0/dP) and $(d\theta/dP)$ for two compositions of the binary Fe-Rh alloy system and for three compositions of the ternary alloy system Fe-Rh-M (M is either Pd or Ir). Our results indicate that (dT_0/dP) is sensitive both to heat treatment and composition.

The existence of a triple point in the P-T phase diagram is demonstrated, giving support to Hargitai's theory[21] that no moment exists on the Rh atoms in the antiferromagnetic state. (This result has also been suggested from the excess magnetic entropy measured by Kouvel[5] and from neutron diffraction work.[15–17]) In essence, his argument is as follows. Knowing the crystal structure and magnetic symmetry of the Fe-Rh alloys in the paramagnetic state, one can calculate from the Landau theory of second-order phase transitions the magnetic states that can be reached by such a transition. Of the possible states, only one exists in which both the Fe and Rh have aligned, nonzero moments; this is the FM state. None of the AFM states has a nonzero Rh moment and one of them corresponds to the structure found for the AFM state by Bertaut *et al.*[17] Hargitai concludes then that if a triple point exists in the P-T plane, above that pressure the AFM-paramagnetic transition is very likely of second order and there can be no moment on the Rh.

Kouvel has recently shown that there is an excess magnetic entropy[5] beyond what can be predicted from Kittel's exchange inversion theory.[22] In this work, we made further comparisons to the exchange inversion model and conclude that it is not applicable. This model assumes two points: (1) that there are two magnetic sublattices of equal magnetization and that the coupling between them is a linear function of some lattice parameter a, (2) that there is a critical value of lattice parameter a_c, where one magnetic state (AFM or FM) is energetically favored for $a<a_c$ and the other for $a>a_c$. From the free energy of such a magnetic system, the equilibrium value of a for both the FM and AFM states is calculated at any temperature. An unstable point is found defining the transition, and the change in volume is immediately given by the difference between a in the FM and AFM states. He also calculates (dT_0/dP) and $(\partial T_0/\partial H)_P$ and relates them through the theory.

II. EXPERIMENT

Hydrostatic pressure was applied to the alloy samples using a piston cylinder apparatus and a pressure transmitting fluid consisting of equal parts of n-pentane and isopentane. Pressures up to 25 kbars and temperatures up to 700°K were obtainable. However, below a pressure of 8 kbar, the higher temperatures were not attempted in order to avoid possible vaporization or chemical breakdown of the pentane mixture. Data at a pressure of 1 bar was obtained using the same experimental setup as for the high-pressure data, but with no pentane mixture present. The magnetic transitions were detected by monitoring the inductance of a coil wound around the sample. This technique provides a very sensitive measurement, as can be seen in Fig. 1.

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The value of the transition temperature is defined in this work as the point where a straight line, extrapolated parallel to the steepest part of the inductance-versus-temperature curve, intersects the measured air-core inductance value of the coil. However, since the curves are the same shape at different pressures, the change in T_0 or θ can easily be found from any point on the curves. Clearly, the accuracy with which a change in transition temperature can be measured is much greater than the accuracy of the temperature itself.

Five samples were prepared and analyzed; all proved to have Fe and Rh compositions within 0.5 at.% of the weighed values and Ir and Pd compositions within 0.05 at.%. The compositions, the values of θ and T_0 at 1 bar, and the values of $(d\theta/dP)$ and (dT_0/dP) are listed in Table I. Also listed for purposes of comparison are the published results of other experimenters. Good agreement in $(d\theta/dP)$ is seen among the binary Fe-Rh alloys; however, the values of (dT_0/dP) from various investigators differ significantly. They range from 4.33–6.3 deg kbar^{-1} and do not demonstrate a consistent pattern with composition.[3,4] Further, no correlation is seen in the binary alloys between T_0 values for various samples of the same or different compositions which were made by different investigators. This problem of comparison of results has been encountered in all the work on Fe-Rh alloys thus far.

In the light of this problem various heat treatments were performed on a given specimen to discover if a variance in T_0 and (dT_0/dP) can be obtained. It was found that for the second composition in Table I ($Fe_{0.472}Rh_{0.528}$) values for (dT_0/dP) from 4.6–5.4 deg kbar^{-1} could be obtained. The lower value was obtained using a 48-h vacuum anneal at 1300°K followed by a slow oven cool. The higher value was obtained by employing a fast water quench after the 48-h vacuum anneal at 1300°K. By the same treatments, T_0 values of 340–315°K were obtained. On the other hand, θ and $(d\theta/dP)$ were apparently not affected by the heat treatment. As a result of this information, we adopted the fast quench heat treatment as a standard in this work and found it to yield very reproducible results.

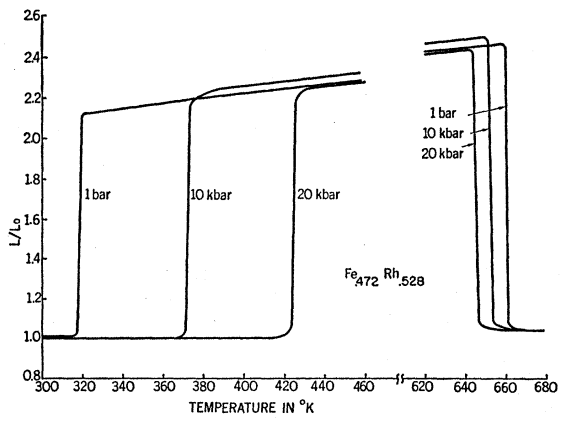

FIG. 1. Ratio of inductance with sample in coil to air inductance versus temperature for $Fe_{0.472}Rh_{0.528}$ alloy water quenched from 1300°K. Data are given for three pressures.

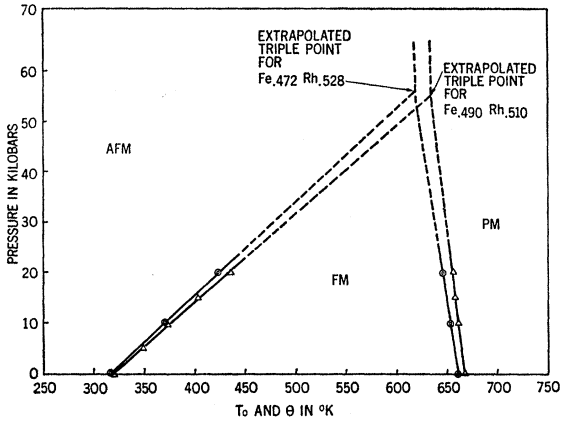

FIG. 2. A triple point in the P-T plane is implied from the data for both binary alloys. The triple points are at pressures and temperatures of 55 kbar and 634°K, and 56 kbar and 617°K, respectively, for the 51.0 and 52.8% Rh samples.

In the ternary alloys, the addition of Ir and Pd raise and lower T_0, respectively.[2,5] A lowering of θ is seen in the Ir specimens but no change occurs in the Pd one. Most interesting, however, are the values of (dT_0/dP) in these ternary alloys. A strong correlation between T_0 and the magnitude of (dT_0/dP) appears to exist, in that the lower T_0 the larger (dT_0/dP). This is an effect not observed for the limited range of T_0 in the binary alloys. As mentioned before, quenching the binary alloys lowers T_0; however, in the Pd ternary alloy, quenching *raises* T_0. This increase in the temperature range over which the FM state exists is consistent with the FM nature of palladium (see, for example, Crangle's work in Ref. 23).

III. DISCUSSION

We suggest that the wide variance in the published values of (dT_0/dP)[3,4,7,20] is primarily due to different heat-treatment histories. From our results it would appear that in the work by Zakharov *et al.*[3] and Ponyatovskii *et al.*[20] an anneal with slow cooling was used, yielding low (dT_0/dP) values. This is further indicated by the width of the transition region shown. (A furnace cool is mentioned explicitly in Zakharov's work.) We would suggest that in the work of Bloch[7] an intermediate cooling rate was probably used, such as an air quench; and Kouvel and Morgan[4] used a very fast quench. In Ref. 5, Kouvel does use a water quench from 1000°C, so it is probable that the same was used in Ref. 4. While no specific quantitative measure of quench rate in deg/sec versus (dT_0/dP) has been made, the qualitative behavior seems to account for all of the measured values.

[23] J. Crangle, Phil. Mag. **5**, 335 (1960).

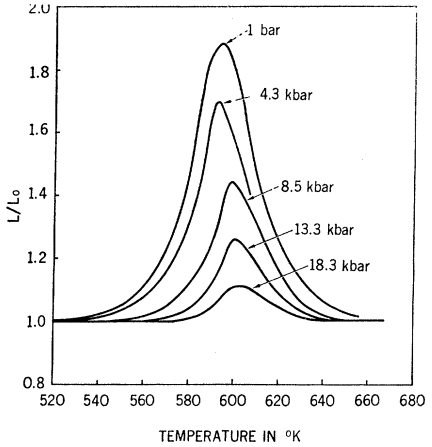

FIG. 3. Ratio of inductance with sample in coil to air inductance versus temperature for $Fe_{0.483}Rh_{0.459}Ir_{0.058}$, showing disappearnce of Fm phase. The slight change in L/L_0 with temperature at 18.3 kbar is felt to be evidence of short-range magnetic order such as is seen just above the Curie temperature in FM metals.

A linear extrapolation of the (dT_0/dP) and $(d\theta/dP)$ values indicates that a triple point should exist in the P-T plane of the binary alloys (Fig. 2) such that above 56 kbars there are only AFM or paramagnetic (PM) phases; the FM phase has been "squeezed out." We have made no measurements at this pressure due to limitations of the equipment. Similar behavior is noted by Ponyatovskii *et al.*[20] This triple point is directly demonstrated for a ternary alloy ($Fe_{0.483}Rh_{0.459}Ir_{0.058}$) as shown in Figs. 3 and 4. Here, because of the high value of T_0 at 1 bar, the FM phase is eliminated at about 15–17 kbar [in spite of the low (dT_0/dP) value]; only short-range magnetic order effects, such as exist above the Curie temperature in ordinary FM materials, appear. At pressures above the triple point, the AFM-PM transition may well be of the second-order Néel type. It would not be expected to be first order if the first-order nature of the AFM-FM transition is attributed to a magnetic exchange inversion effect.[22] This is because the discontinuous volume change is directly related to the square of the sublattice magnetization in this theory; and near the Curie (or Néel) point, this magnetization becomes vanishingly small. Hence, the volume change should correspondingly go to zero at the triple point and the second-order transition prevail at higher pressures.

The possible existence of a second-order transition at pressures above the triple-point pressure is consistent with Hargitai's argument,[21] in which he uses the Landau theory of second-order transitions to show that there is no moment on the Rh atom in the AFM state. This same conclusion, that there is no Rh moment, is also suggested from the neutron diffraction results of Shirane *et al.*[19] and from the work of Kouvel.[5] However,

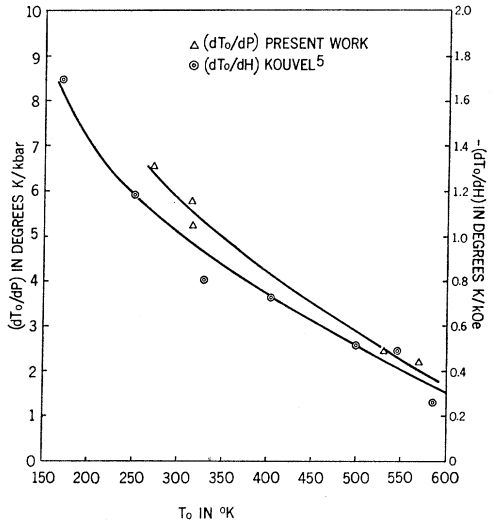

FIG. 5. (dT_0/dP) and (dT_0/dH) versus T_0, showing approximate constancy of the ratio of the pressure and field dependences of T_0.

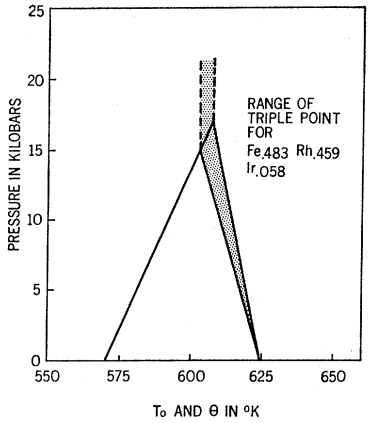

FIG. 4. P–T diagram showing disappearance of FM phase at 15–17 kbar. The width of the Curie temperature line indicates the experimental uncertainty.

more conclusive experiments, such as x-ray diffraction, differential thermal analysis, or resistance measurements, done under high pressure at high temperatures, are necessary to establish or rule out the second-order nature and hence the applicability of Hargitai's theory. In fact, a recent nonhydrostatic experiment performed by Leger, using differential thermal analysis on an $Fe_{0.50}Rh_{0.46}Ir_{0.04}$ alloy, shows that above the triple point the AFM-PM transition is first order.[24] If one can ignore the effect of shear on the transition, this may well show that the pure Fe-Rh alloy has a first- and not a second-order transition at pressures above the triple point.

The growing evidence that no moment exists on the Rh atom in the AFM state, that the AFM-PM transi-

[24] J. M. Leger (private communication).

tion above the triple point may be first order,[24] and that an anomalously large magnetic entropy is associated with the FM-AFM transition,[5] indicates quite strongly that the exchange inversion model is not applicable to the Fe-Rh alloy system. A further difficulty with the model arises in the stated assumption that the magnitude of the sublattice magnetization M is to be considered as independent of the interlattice interaction. In fact, there are four magnetic sublattices in these alloys, two Fe and two Rh, but they are not all relatively unaffected by the transition. The constancy of M is a reasonable assumption for Fe, where the moment per atom is known to decrease by less than 10% (from 3.30–3.04 μ_B) when going from the AFM to the FM state.[19] However, for the Rh sublattice, a change in the moment per atom to zero from 1.0 μ_B per atom[19] may occur. Clearly then, the Rh sublattice magnetization would not be approximately constant nor should it be expected to be. Even if the Rh moment is not zero in the AFM state, it is small and the location of the Rh atom is in the center of eight Fe atoms four tetrahedrally arranged about it with positive spin and four with negative spin.[5,17] Thus, any small moment the Rh might have probably would not be ordered in this magnetic state due to the zero net exchange interaction.

Even if the exchange inversion model can be modified by using the appropriate value of M for the various sublattices, or perhaps by neglecting the Rh entirely, a question arises regarding what the proper unit cell volume change ΔV is because ΔV is related to the sublattice magnetization by

$$\Delta V = 2\rho M^2/R. \tag{1}$$

Here R is the elastic stiffness constant divided by the square of the lattice parameter and $\rho = (\partial\alpha/\partial V)$, the volume derivative of the molecular field constant connecting the sublattice magnetizations. Both are approximately constant over the range of pressures (or volumes) encountered. However, it is possible that ρ has very different values for Fe-Fe and Rh-Rh sublattice interactions and that the relative magnetizations are *controlled* by this restriction on ΔV shown in Eq. (1). This does not, however, seem to be a very satisfactory solution to this point.

One additional comparison to the exchange inversion theory can be made in the following way. From the general thermodynamic relations $(\partial T_0/\partial H)_P = -(\Delta M_s/\Delta S)$ and $(\partial T_0/\partial P)_H = (\Delta V/V\Delta S)$, it follows immediately that

$$(\partial T_0/\partial H)_P = -(V/\Delta V)\Delta M_s(\partial T_0/\partial P)_H. \tag{2}$$

Here ΔS is the change in entropy at the transition and ΔM_s is the change in saturation magnetization. Using the $(\partial T_0/\partial P)_H$ values obtained in this work and the $(\partial T_0/\partial H)_P$ data of Kouvel,[5] $-(V/\Delta V)\Delta M_s$ can be calculated using only thermodynamics. An equivalent expression can be derived from the exchange inversion theory in terms of the sublattice magnetizations. For the case of two magnetic sublattices and only one lattice parameter a being of importance to the first-order transition, the relation is[22]

$$(\partial T_0/\partial H)_P = -(aR/\rho M)(\partial T_0/\partial P)_H. \tag{3}$$

Deriving the above expression for a three-dimensional case and n equally magnetized sublattices, one obtains

$$(\partial T_0/\partial H)_P = -(VRn/2\rho M)(\partial T_0/\partial P)_H, \tag{4}$$

where V again is the volume of a unit cell. Using the expression given from the theory for the difference in volume between the ferromagnetic and antiferromagnetic states,

$$\Delta V = V_{FM} - V_{AFM} = 2\rho M^2/R, \tag{5}$$

one obtains the expression

$$(\partial T_0/\partial H)_P = -(V/\Delta V)nM(\partial T_0/\partial P)_H, \tag{6}$$

which is equivalent to Eq. (2) with nM replacing ΔM_s. From this, nM can be calculated for any Fe-Rh alloy.

In Fig. 5, it is apparent that the ratio of (dT_0/dH) to (dT_0/dP) is approximately constant and is -0.175 bar/Oe. This implies that $(V/\Delta V)nM$ would have to be a constant for all T_0. Using $\Delta V/V = 9\times10^{-3}$ at 330°K,[3,12,14] Eq. (6) gives a value of nM (or ΔM_s) of 20 kG; the saturation magnetization at this temperature is about 15 kG. Considering the approximate nature of the calculation, this agreement of the thermodynamics is good and adds confidence to the measured values. However, it must be remembered that the calculation of nM from Eq. (6) was performed, assuming equal magnetizations in each sublattice. If one naively assumes that this is true (in spite of what is known about the Rh) an M of 5 kG is obtained for each sublattice. On the other hand, if one considers the measured magnetization and distributes it by the ratio of moments, Fe has about 6 kG per sublattice but Rh only about 1 kG in the FM state or zero in the AFM state. While the Fe number agrees with the 5 kG from the theory, it does not agree at all with the means of obtaining it (using $n=4$).

Hence, the theoretical picture for explaining the magnetic behavior of Fe-Rh alloys in this concentration range is not clear. Apparently, the exchange inversion model cannot be invoked in this case because of the excess magnetic entropy, the likely absence of a moment on the Rh in the AFM state, and the lack of agreement with the confirmed prediction of thermodynamics; an entirely new model must be found.

ACKNOWLEDGMENTS

The author would like to thank Dr. G. A. Samara and Dr. D. H. Anderson for useful and stimulating discussions. Excellent experimental assistance was provided by B. E. Hammons and a sample analysis by R. G. Dosch. The samples were fabricated by R. J. Baughman.