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The Paramagnetism of Dissolved Mn in α and β Brasses

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by

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Abstract:

Paramagnetic susceptibility measurements have been made on α and β brasses containing $\sim$ 1 w/o Mn. The susceptibility varied with temperature according to the Curie Weiss law and the Curie constant and thereby the Bohr magneton number per Mn atom were determined. Interpreted in terms of valency, Mn monovalent in copper has a valency in α brass which decreases progressively with zinc content attaining the value 0.58 at the limiting α composition. Mn in β brass exhibits a valency 0.8. These results are not in keeping with previous values for the valency of manganese as determined from phase boundary relationships and electron to atom ratios.

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Introduction.

The results described in this paper apply to the paramagnetic properties of small amounts ~ 1 to 1.5 w/o of manganese dissolved in α brasses of varying composition and in β brass. Measurements have been made in the temperature region between -100 °C and +200 °C where one expects, by analogy with the copper manganese system, a Curie Weiss paramagnetism to occur. Lack of appropriate cryostats prohibited measurements at very low temperatures but such measurements would be interesting in the light of the anamalous behaviour found in binary copper manganese alloys.

Much attention has been given to the concept of valency for a transition metal in a noble metal or alloys of noble metals and different methods have been used to determine this quantity but that based on a measurement of the paramagnetic properties of the transition metal atom is probably the most direct. In particular several independent magnetic studies of the copper manganese system have been made by Gustafsson (1936), Néel (1932), Myers (1956) and good evidence is available that small amounts of Mn dissolved in Cu have a Bohr magneton number p_{eff} equal to or very nearly equal to 4.9 that value which for spin only paramagnetism corresponds to six 3d electrons per Mn atom or a valency of 1.

Hume-Rothery (1948) studied the effect of Mn on the $\alpha/\alpha + \beta$ phase boundary of brass and concluded from the known dependence of this boundary on electron to atom ratio that it was divalent when dissolved in brass. Later, Hume-Rothery and Howarth, (1952), using the same method, deduced a value 1.83 to 1.93 for the apparent valency of manganese from measurements of the $\alpha/\alpha + \beta$ and $\beta/\alpha + \beta$ boundaries in the Cu-Zn-Mn and Cu-Al-Mn systems. It is to be noted that the valency was essentially the same whether the manganese was dissolved in the α or β phase; furthermore it was independent of the manganese concentration over the interval 0 to 10 $^{a}/o$.

The difference in behaviour between manganese in copper and manganese dissolved in α brass is striking. We can expect that, to a good approximation, pure copper and the primary solid solution of zinc in copper should provide similar matrices for the solution of small amounts of manganese; the principal differences being the larger atomic spacing and the greater electron to atom ratio of the alloy in the neighborhood of the $\alpha/\alpha + \beta$ phase boundary.

Hume-Rothery and Howarth's results imply that the apparent valency of manganese in a noble metal alloy should increase as the electron to atom ratio increases. On the other hand, Jones (1955) has concluded that the number of electrons in the 3d configuration of a transition metal atom increases steadily with the electron concentration in the valency band of the alloy. The measurements described in this paper were made to study the apparent valency of manganese when dissolved in α brasses of different electron to atom ratios. Measurements were also made on specimens of β brass.

Experimental procedure.

Alloys of manganese in brass were made by melting portions of a master alloy of copper and manganese with different amounts of zinc.

The materials used were Matthey spectrographically standardised copper, zinc and manganese.

The master alloys containing between 1 - 2 w/o Mn were melted under vacuum in pure alumina crucibles by induction heating. The melts were bottom poured into a split copper mould. Thereafter weighed portions of the master alloy were, together with weighed amounts of zinc, melted under an argon atmosphere in sealed quartz ampoules. The manganese brasses so formed were then hammered and annealed under an argon atmosphere in sealed quartz tubes at 650 °C for periods varying from 3 to 6 days. Specimens for metallographic, magnetic and chemical analyses were machined from the annealed ingots. Specimens were used in the quenched state.

The resultant brasses contained between 0.7 to 1.5 w/o Mn. Magnetic measurements were made using a modified Sucksmith balance, Lundquist & Myers (1962). Measurements were not made above 200 °C due to the small susceptibilities found at higher temperatures.

Results.

After homogenisation of the alloys specimens for magnetic, metallographic and chemical analyses were prepared from the middle part of each ingot. For convenience the alloys are numbered 1 to 10. Metallographic analyses showed the alloys to be clean and homogeneous. Alloys 1 to 7 were wholly in the α phase, alloys 8 and 9 contained mixed $\alpha + \beta$ and alloy 10 was pure β. In the magnetic measurements although four different values of field strength were always used no dependence of susceptibility on field strength was observed and no correction for ferromagnetic impurity required.

The measured susceptibilities were corrected for the diamagnetism of the matrix, the latter being determined from Henry & Rogers (1956) values for the diamagnetic susceptibilities of pure brasses. All the alloys were paramagnetic the susceptibility obeying the Curie Weiss law. The Curie constant C and hence the effective Bohr magneton number p_{eff} were determined from Curie Weiss plots. Table 1 summarises the results.

In these measurements there are two principal sources of error namely the correction for diamagnetism and the uncertainty in the determination of the manganese content. Besides these any error in determining the paramagnetic susceptibility is insignificant. We can do little about the correction for diamagnetism. All alloys were carefully analysed for all components particular care being paid to the determination of manganese which in the small amounts used in these alloys is estimated accurate to $\pm$ 2 %. Errors in the evaluation of the Curie constant are halved when calculating p_{eff} since $p_{eff} \alpha \sqrt{C}$ and we believe that our p_{eff} values are (excluding the factor due to uncertainty in the diamagnetism) correct to at least $\pm 0.1\ \mu_B$ and probably correct to $\pm 0.05\ \mu_B$.

The Curie temperature, Θ, was positive in all alloys. Some spread in the Θ values is evident but this quantity is more difficult to determine accurately from high temperature measurements than the Curie constant.

TABLE I

Alloy	Composition: Weight % Cu	Weight % Zn	Weight % Mn	Atom % Cu	Atom % Zn	Atom % Mn	Electron to atom ratio of alloy	Curie Constant: gm alloy	Curie Constant: gm atom Mn	p_{eff} (μ_B)	Θ (°K)
1	99.0	-	1.00	98.86	-	1.14	0.999	$5.27_5 \cdot 10^{-4}$	2.90	4.83	21
2	90.0	9.0	0.91	90.2	8.76	1.06	1.087	$4.80 \cdot 10^{-4}$	2.90	4.83	27
3	86.0	13.2	0.89	86.1	12.85	1.03	1.127	$4.60 \cdot 10^{-4}$	2.84	4.78	25
4	79.1	19.0	1.56	80.2	18.1	1.83	1.180	$8.05 \cdot 10^{-4}$	2.82	4.77	31
5	74.9	23.7	1.09	75.5	23.2	1.27	1.229	$5.46 \cdot 10^{-4}$	2.75	4.70	35
6	67.9	31.5	0.70	68.4	30.8	0.81	1.305	$3.33 \cdot 10^{-4}$	2.62	4.59	25
7	65.7	33.0	1.28	66.2	32.3	1.49	1.322	$6.00 \cdot 10^{-4}$	2.57_5	4.55	28
8	61.0	38.0	1.22	61.4	37.4	1.42	1.371	$5.66 \cdot 10^{-4}$	2.54_4	4.52	27
9	58.1	40.5	1.16	58.6	40.0	1.36	1.396	$5.62_5 \cdot 10^{-4}$	2.67	4.64	32
10	49.4	49.5	1.00	50.1	48.8	1.17	1.486	$5.00 \cdot 10^{-4}$	2.74_5	4.70	28

Discussion.

Before proceeding to a discussion of the manganese brasses we wish to comment on the paramagnetism of the binary manganese copper alloy. As pointed out by Schmitt & Jacobs (1957) considerable confusion has occurred in the discussion of the paramagnetic properties of the dilute alloys of manganese in copper by assuming, and wrongly so, that the number of electrons contributing to the magnetic moment is equal to the p_{eff} value; thus several authors have assumed there to be five holes in the 3d shell of manganese because $p_{eff} \sim 4.9$. The magnetic data of Gustafsson, Néel & Myers and that presented here is overwhelmingly in favour of assigning p_{eff} the value $\sim 4.9 \pm 0.1$, that value which, for spin moment only, corresponds to an atomic moment of 4 Bohr magnetons and an atomic configuration $3d^6 4s^1$. Thus small amounts of manganese in copper exhibit a valency ~ 1. Furthermore this valency as measured via the paramagnetic properties Myers (1956) changes little even for manganese contents as high as 20 $^a/o$. These results may be considered in terms of Friedel's (1956) model of virtual bound states for the d electrons of transition metals dissolved in noble metals.

Friedel in discussing the magnetic and electrical properties of dilute solutions of transition metals in copper has proposed broadened or "virtual" bound states with positive energy in the region of the Fermi limit resonating with but not contributing to the conduction band. For manganese in copper the magnetic data require the ten 3d states per atom to be split into two sets of virtual bound states each set containing five states of given spin. Thus for a dilute alloy where the interaction between transition metals is weak the situation may be pictured as in fig. 1. . One half of the virtual states all with the same spin lie well below the Fermi limit, and the upper half has begun to cross this limit so that approximately four states per atom lie empty above the conduction band. Since the manganese is monovalent in this system, replacing copper by manganese will not change the electron content of the conduction band; thus unless the effects of lattice expansion and manganese interactions are significant there will be little change in the situation pictured in fig. 1 as the manganese content is increased. The experimental data are in agreement with the assumption that the effects mentioned are not large until the manganese content approaches about 20 % manganese.

Returning to the properties of the manganese brasses fig. 2 shows the variation of p_{eff} as a function of electron to atom ratio for the alloy. Replacing copper by zinc increases the electron concentration of the alloy and if the empty bound states are uniformly distributed in energy one would expect the p_{eff} value to decrease in a manner dependent upon the form of the conduction band leading to an initial decrease which is more rapid than that found at the limiting α brass composition. In fact the opposite is found to occur, little change in the p_{eff} value occurring up to compositions containing 20 ^{a}/o zinc and the decrease becoming most pronounced as the phase boundary is approached. We therefore imply that the energy distribution of the bound states is not uniform; furthermore the broadening of the levels is dependent upon the depth of the occupied portion of the conduction band; these effects must be present to account for the observed variation. Clearly with such a model, for a given alloy electron concentration, the valency of the manganese should be dependent upon the manganese content of the alloy; it appears however that the range of manganese contents used in the present experiments has insignificant effect.

The manganese valencies calculated from the p_{eff} values are also shown in the upper curve of figure 2 where it is seen that it decreases from a value near to unity in a copper matrix to the value 0.58 appropriate to the limiting α composition. Manganese dissolved in the pure β brass phase has according to our results a valency 0.8 and the change in occupancy of the broadened 3d states must be attributed to the alteration in the energy band structure associated with the phase change. The value 0.8 is close to that found for manganese in the Heusler alloys.

Although it is very doubtful whether a quantitative vindication of the above model is at present possible it provides a feasible qualitative description of our results. As will have been noticed our conclusions concerning the valency of manganese in α and β brasses are not in keeping with the findings of Hume-Rothery & Howarth.

Acknowledgements.

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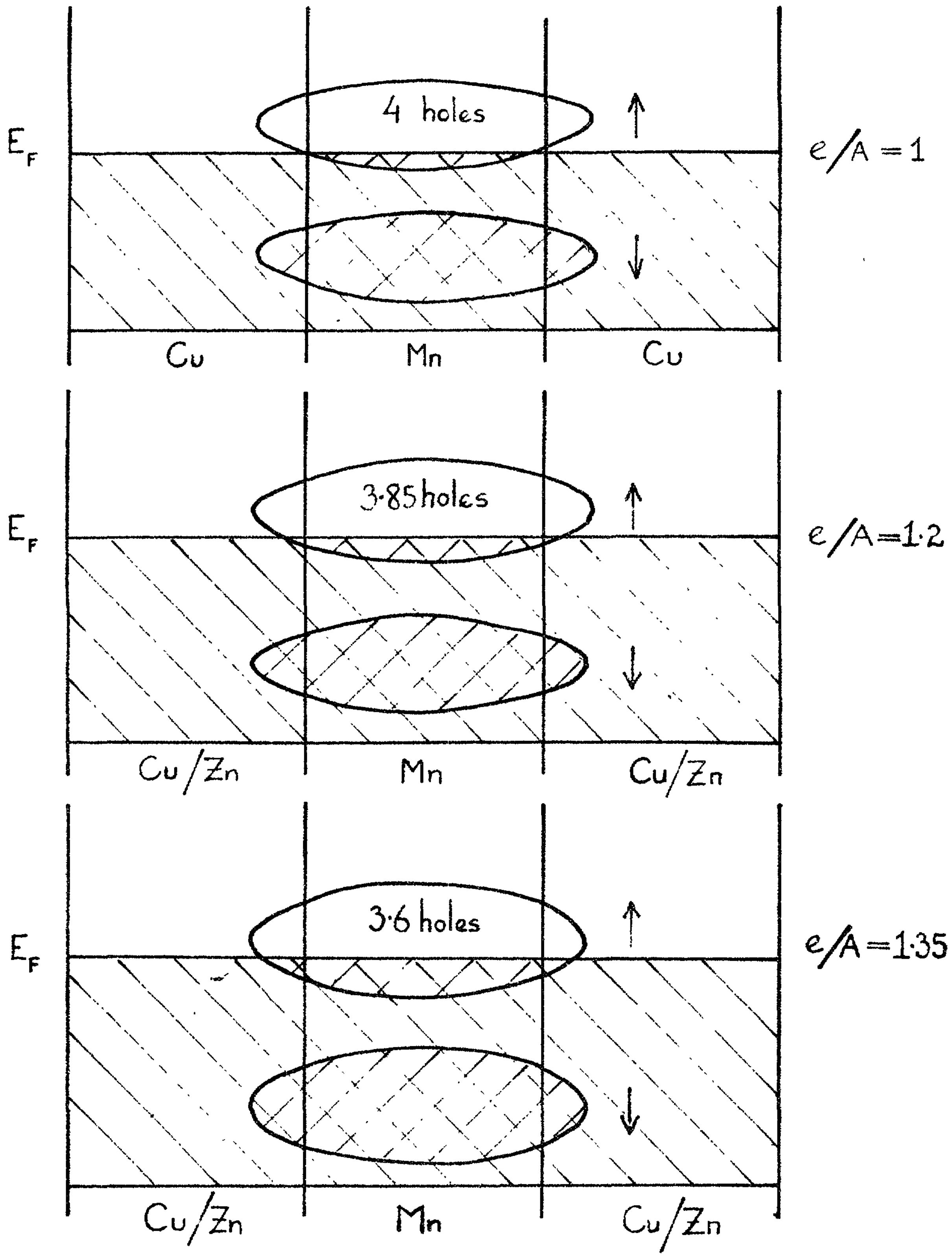

Fig. 1. Friedel's model of virtual bound states; these states are shown filled to the level demanded by the paramagnetic susceptibility at different electron to atom (e/A) ratios.

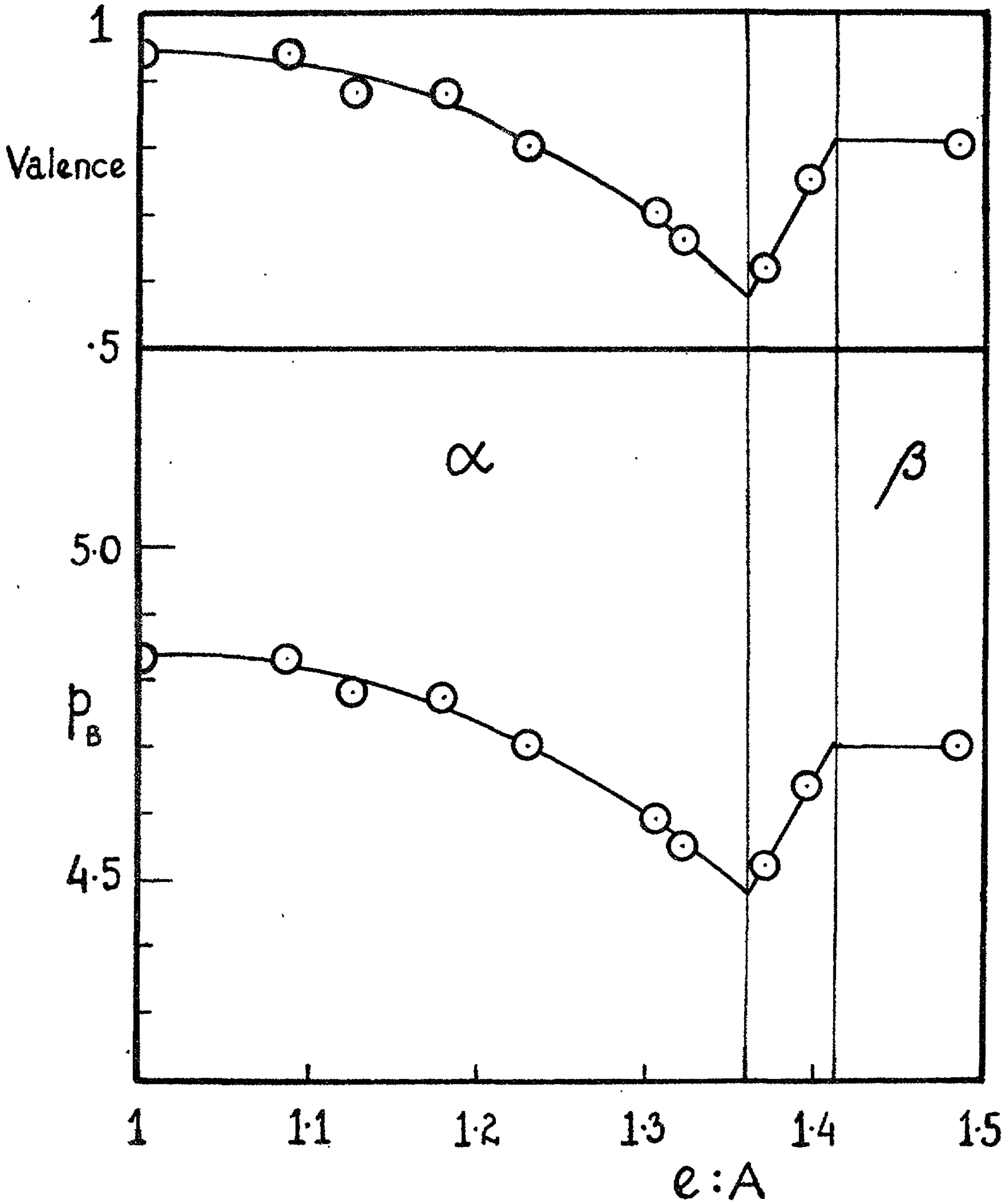

Fig. 2. The variation of the effective Bohr magneton number and the derived apparent valence for Mn with electron to atom ratio of the alloy.

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