

CONNECTION BETWEEN STRUCTURAL AND MAGNETIC PARAMETERS OF THE TRANSITION METALS

F. M. GAL' PERIN

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The connection between the structural parameters (type of lattice, interatomic distances, coordinational number, etc.) and the magnetic parameters (atomic magnetic moment, Curie point, Curie constant) is considered for the pure transition elements Cr, Mn, Fe, Co, and Ni as well as for a number of their ferromagnetic ordered alloys and chemical compounds. These relations and the available experimental data on the crystalline and electronic structures of the metals are used to compute the magnetic parameters, which are found to be in good agreement with the experiments.

AFTER a detailed analysis of extensive experimental material, we noted the close connection between the structural and magnetic parameters of ferromagnets, which we expressed by means of semi-empirical relationships.^{1,2} The latter, in conjunction with known optical data on the crystalline and electronic structures of the ferromagnets, were used to calculate the magnetic parameters of pure ferromagnetic metals, of the same metals in their alloys, and finally of the alloys themselves; the agreement with experiment was satisfactory.

Recent years have brought to light many new facts in ferromagnetism. Neutron-diffraction investigations have shown that the use of the Heitler-London-Heisenberg approximation (along with its natural extension, the polar model of Shubin and Vonsovskii) is more suitable for the description of the interaction of the internal electrons (*d*) in ferromagnets than the collective-electron model (cf., e.g., references 3-6). Furthermore, neutron-diffraction and x-ray methods have shown that the electron structure of transition metals differs greatly from that previously suggested in the literature.⁷⁻¹⁰

In the present paper we attempt to improve the equations proposed by us for the purpose of (a) taking account of the results of the aforementioned new research and (b) extending these equations to include other transition metals (Cr and Mn) in the paramagnetic and ferromagnetic states, and not merely Ni, Co, and Fe in the magnetic state, as done essentially in the earlier investigations. In the first part we develop the concepts underlying the aforementioned relations. These are then applied to pure ferromagnetic metals and to their ordered alloys, and finally to Mn and Cr in ferro-

magnetic chemical compounds with a structure of the NiAs type and to Mn in ordered Geisler alloys of the type MnCu₂Al.

1. PRINCIPAL PREMISES

We consider the transition elements of the first long period of the periodic table, with atomic numbers *Z* from 21 to 29. Each of these is characterized by a constant, derived by us, which has the dimensionality of a length, equal to (Angstroms)

$$R = 0.13 [(Z/2)^2 - 14.75Z + 235.5] \quad (\text{for } Z \geq 26), \quad (1)$$

$$R = 0.13 [(Z/2)^2 - 13.75Z + 209.5] \quad (\text{for } Z \leq 26). \quad (2)$$

For lattices of metals of type A2 (cubic volume-centered, as in Fe) and of type A3 (hexagonal close-packed, as in Co) one considers in the general case the first and second coordination zones of the lattice (*i* = 1 and *i* = 2, where *i* is the number of the zone).

We denote the interatomic distance and the number of neighbors of the atom by *r*₁ and *n*₁ for the first zone and by *r*₂ and *n*₂ for the second; *n*₁ = 8 and *n*₂ = 6 for lattices of type A2, and *n*₁ = *n*₂ = 6 for lattices of type A3. In the nearest-neighbor approximation, only the first zone is considered. An exception is Co, for which the neighbors of the second zone are also the nearest (because *r*₂ ≈ *r*₁). For lattices of type A1 (cubic face centered, as in Ni) only the first zone was considered (*n*₁ = 12) because *r*₂ = *a* >> *r*₁ (*a* is the lattice parameter).

We introduce the concept of the "effective" interatomic distance *r*_{eff} = *r*_{*i*} - *R*, where *r*_{*i*} is the equilibrium interatomic distance in the *i*-th zone. This concept is introduced so as to take into account, in the calculation of the magnetic param-

TABLE I. Structural Parameters of Ni, Co, and Fe

Metal (lattice type)	$n_1(r_1, \Delta)^{[1]}$	$n_2(r_2, \Delta)^{[1]}$	$R, \text{ \AA}$	Class of metal	$r_1 - R, \text{ \AA}$	$r_2 - R, \text{ \AA}$	Δ	Δ_0	$N_d (n_s)$
Ni (A1)	12(2.486 ₈)	—	2.408 ₂	2	0.078 ₆	—	0.605 ₂	0.605 ₂	2 (2)
Co (A3)	6(2.49 ₆)	6(2.50 ₇)	2.53 ₈	1	-0.03 ₉	-0.03 ₁	0.26 ₆	0.26 ₈	3 (2)
Fe (A2)	8(2.477 ₇)	6(2.861 ₀)	2.733 ₂	1	-0.255 ₅	0.127 ₈	1.805 ₆	1.313 ₆	4 (2)

eters, only the magnetic electrons (of the unfilled electron shells that participate in the magnetism; the nonmagnetic electrons of the filled shells are also located at the interatomic distance r_1).

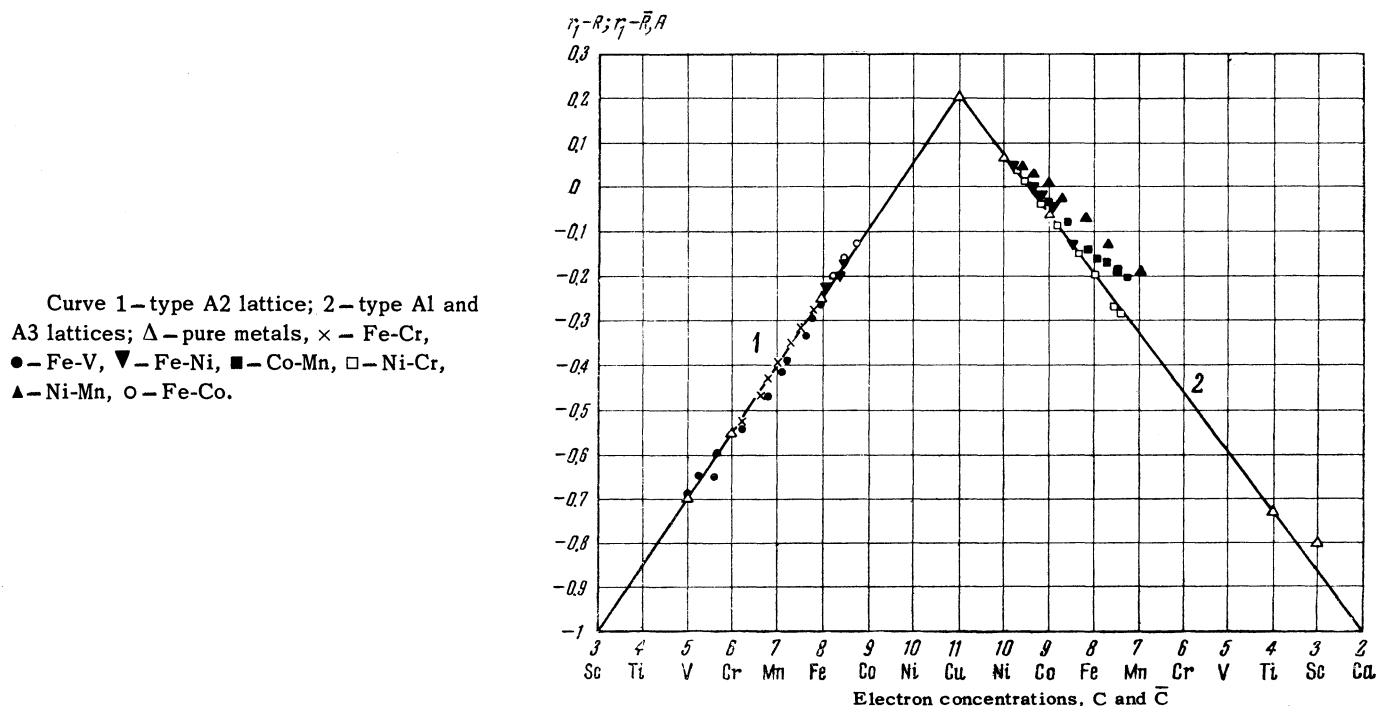
It is seen from Table I that the difference $r_1 - R$ is quite small for pure ferromagnetic metals.

Pure metals can be divided into two classes, depending on the sign of the difference $r_1 - R$. The first class (1) contains the metals (Co, Fe, Mn, and so on) for which this difference is negative, while the other (2) contains those (Ni etc) with a positive difference. This grouping of metals explains many experimental facts (see below).

Let us consider the law that governs r_{eff} . Let the abscissa (see the figure) represent the concentration C of the electrons (the number of the s and d electrons) of the isolated atom, first in ascending order (from $C = 3$ for Sc to $C = 11$ for Cu, left segment of the axis), followed by a descending order (right segment) along the same axis. Let the ordinates represent the difference $r_1 - R$. We plot the corresponding points for type A2 lattices over the left segment, and those for types A1 and A3 over the right segments. This results in the triangle shown in the figure.

An analogous picture is observed also for many binary ordered alloys of transition elements. The figure shows the dependence of the effective interatomic distance in the alloy lattice, $\bar{r}_{\text{eff}} = r_1 - \bar{R}$, on the mean concentration of the electrons of the alloy atom, $C = \lambda_a C_a + \lambda_b C_b$, where C_a and C_b are the concentrations of the electrons of the atoms of components a and b; λ_a and λ_b are the atomic concentration of the latter in the alloy; r_1 is the equilibrium interatomic distance in the first zone of the alloy lattice (it depends on the concentration of the alloy); $\bar{R} = \lambda_a R_a + \lambda_b R_b$; R_a and R_b are constants of the components a and b, calculated from (1) and (2). It is seen from the figure that the points of the alloys under consideration lie as a rule on the same triangle. Exceptions are certain alloys, particularly of manganese (Co-Mn, Ni-Mn, and others), whose points deviate from the triangle.

Along with the effective interatomic distance, one must consider also the number of neighbors of the atom in zone i , n_i ; we introduce for this purpose the quantity $\sum n_i |r_1 - R|$, which has the dimension of length. The change in the number Δ of magnetic electrons of the atom (with uncompen-



sated spins) corresponding to this quantity, a change due to the fact that the outer portion of its electron shell (*s* and *d*) is substantially deformed in the crystalline state (compared with the shell of the isolated atom), is equal to*

$$\Delta = 0.642 \sum n_i |r_i - R|. \quad (3)$$

In the nearest-neighbor approximation we use instead of (3)

$$\Delta_0 = 0.642 n_1 |r_1 - R|.$$

An exception is Co, for which Δ is used in this approximation, and not Δ_0 (because $r_2 \approx r_1$).

It will be shown below that Δ or Δ_0 enters into the relation for all magnetic parameters, thus connecting the latter with the structural parameters.

Let us dwell on the question of the electronic structure of the considered transition elements, a structure which must naturally be taken into account when formulating the foregoing relations.

Isolated atoms of these elements, with the exception of Cr, have two *s* electrons each (Cr has one *s* electron) and either five (Cr, Mn), six (Fe), seven (Co), or eight (Ni) *d* electrons. The question of the distribution of these electrons in the atoms of the same elements in the crystalline state (transition metals) has been under discussion for many years.¹² It follows from recent experimental x-ray data⁷ that the number of *d* electrons per atom of the metal is 0.2 ± 0.4 for Cr (A2), 2.3 ± 0.3 for Co (A3), 9.7 ± 0.3 for Ni (A1), and 9.8 ± 0.3 for Cu (A1). We see, first, that the electron distribution in a metal with an A2 lattice differs greatly from the distribution in isolated atoms: the *d* shell contains few electrons,[†] their number being equal to the number of

*The coefficient 0.642 in (3) is justified by the following reasoning. Co and Ni have the same coordination numbers (12) and practically equal interatomic distances (2.50 and 2.49 Å). However, their constants *R* (2.54 and 2.41 Å) differ by 0.13 Å, and the number of *d* electrons of their atoms differ by 1. On this basis, we propose the following generalization to include metals with arbitrary types of lattices, interatomic distances, and coordination numbers: when the interatomic distance r_1 in the lattice of a metal with coordination number 12 is reduced by 0.13 Å, the number of electrons of the atom is reduced by 1, and if the interatomic distance is reduced not by 0.13 Å, but by $(r_1 - R)$, for the same number of nearest neighbors, the number of its electrons changes by an amount $(r_1 - R)/0.13 = 7.7 (r_1 - R)$. The resultant quantity, referred to one neighbor of the atom, is $7.7 (r_1 - R)/12 = 0.642 (r_1 - R)$: referred to n_1 neighbors it becomes $0.642 n_1 (r_1 - R)$. This is analogous to (3).

†Lomer and Marschall⁸ believe that the remaining *d* electrons have shifted to the *s* and *p* levels, thus accounting for the large number of conduction electrons, whereas in metals with A1 and A3 lattices there are few such electrons (because the *s* electrons go to the *d* shell).

Bohr magnetons (M_B) comprising the magnetic moments *m* of the atoms ($m = 2.20 M_B$ for Fe; according to neutron-diffraction data,¹⁰ Cr is antiferromagnetic with an antiferromagnetic moment $m_{af} = 0.40 M_B$),* the *d* shell contains electrons of only one spin orientation. Second, the *d* shell of a metal with A1 or A3 lattice contains many electrons, $10 - m$ in number, where $m = 1.71$ for Co and 0.60 for Ni. A considerable portion of the *s* electrons, belonging to the *s* shell of the isolated atoms prior to formation of the crystal, shift to the *d* shell of the metal, and the electrons in the latter form two groups with opposite spin orientation.

Let us proceed to examine the connections between the foregoing crystal-structure, electron-structure, and magnetic parameters.

2. MAGNETIC PARAMETERS

Ferromagnetic Atomic Magnetic Moment

We first revise the concept of the number of electrons with uncompensated spins, participating in the spontaneous magnetization (ferromagnetic electrons¹³). The theory usually employs approximations for which *e* is an integer. For example, in the Bloch-Moller formula for the "three-halves" law, $e = 1$ for Ni and $e = 2$ for Fe.¹⁴ In the experiments, however, judging from the new data on the electronic structure of pure ferromagnetic metals⁷ and from their atomic magnetic moments, *e* becomes equal to *m* and is fractional. The same can be said of σ , the number of electrons that contribute to the paramagnetic moments of the same metals ($\sigma = 2.30$ for Fe, 0.90 for Ni, etc.). We shall give equations for both σ and *e*.

We write $n_d = C - n_s$, where $n_s = 2$ for all transition metals; $N_d = 10 - n_d$ for $n_d \geq 5$, and $N_d = n_d$ for $n_d < 5$ (see Table II). It is seen from the table that in the case of a ferromagnetic metal the integer portion m_0 of the experimental value of *m* is as a rule equal to $N_d - n_s$. Thus, $m = N_d - n_s + \epsilon$, where ϵ is the fractional increment of the moment (in M_B units), oriented, naturally, parallel to the integer portion of the moment [since $m > (N_d - n_s)$].

We note that $N_d - n_s = 2$ for Fe; on the other hand, the integral number of the electrons actually in the *d* shell, according to reference 7, is also equal to 2. Finally, in the Bloch-Moller formula, $e = 2$ for Fe. We assume that for all transition metals, which, like Fe, belong to the first class of metals, $e = N_d - n_s$ ($e = 1$ for Co, $e = 2$ for

*We shall drop henceforth the symbol M_B for the sake of brevity, since the magnetic moment is always expressed in units of M_B .

TABLE II. Atomic Magnetic Moments of Metals and Alloys

Metal	Lattice type	<i>m</i>	<i>m_s</i>	<i>N_d</i>	<i>N_d - n_s</i>	<i>ε</i>	<i>m</i> , cal- culated
		Experiment					
Ni	A1	0.60*	0	2	0	0.60	0.60
Co	A3	1.71	1	3	1	0.69	1.69
Fe	A2	2.20	2	4	2	0.20	2.20
Fe (FeCo)	A2	2.80	2	4	2	0.96	2.96
Co (FeCo)	A2	1.98	1	3	1	0.96	1.96
Fe (Ni ₃ Fe)	A1	2.97	2	4	2	1.04	3.04
Ni (Ni ₃ Fe)	A1	0.62	0	2	0	0.51	0.51
Ni (Ni ₃ Mn)	A1	0.30	0	2	0	0.69	0.69
Mn (Ni ₃ Mn)	A1	3.18	3	5	3	0.55	3.55
Mn (MnAs)	NiAs	3.40	3	5	3	0.37	3.37
Mn (MnSb)	NiAs	3.53	3	5	3	0.55	3.55
Mn (MnBi)	NiAs	3.52	3	5	3	0.53	3.53
Cr (CrSb)	NiAs	2.70	2	4	2	0.71	2.71
Cr (CrTe)	NiAs	2.40	2	4	2	0.45	2.45
Cr (CrO ₂)		2.07	2	4	2	—	—
Mn (MnCu ₂ Al)	A2	4.10		5	3	1.07	4.07
Mn (MnCu ₂ Sn)	A2	4.10		5	3	1.07	4.07
Mn (MnCu ₂ In)	A2	4.10		5	3	1.07	4.07

Number of electrons participating in the paramagnetism**

Ni	A1	0.9	0	2	0	0.89	0.89
Co	A3	2.30		3	1	1.30	2.30
Fe	A2	2.30	2	4	2	0.30	2.30
Mn (MnAs)	NiAs	3.60	3	5	3	0.60	3.60
Mn (MnSb)	NiAs	3.20	3	5	3	0.20	3.20

*The values are rounded off; the exact ones are given in the text.

**The lower part of the table differs from the upper only in that the 3d, 4th, and 8th columns contain the number of paramagnetic electrons, σ , instead of the number of ferromagnetic electrons, m .

Fe, $e = 3$ for Mn, etc.), and for metals like Ni, which belong to class 2, $e = 1$, i.e., when writing the relation for the number, e , we start with its value as given by the Bloch-Moller formula, which at present gives the most accurate results.*

Going to the relation for the fractional added term ϵ , we consider that, according to the theory of Vonsovskiĭ and Vlasov,¹⁵ the atomic magnetic moment of pure ferromagnetic metals is

$$m = N_d + 0.15n_s(J_0/J - 4)/(1 - 2J_s/J), \quad (4)$$

where J_0 and J are the exchange integrals between the s and d electrons in one lattice site and between its neighboring sites, respectively, and J_s is the transfer integral of the s electron. At the present state of the theory, as pointed out by the authors of the theory itself, these integrals

*In view of the fact that a minimum number of arbitrary model assumption has been made in the derivation of this formula from the multi-electron spin-wave theory, Landau and Lifshitz have therefore proposed to evaluate the volume integral A by the Bloch-Moller formula, and not by rough approximate formulas (of Heisenberg and others), in which A is connected with the Curie point. The relation which we derived from this point of view for A (in particular, with allowance for the proposed relation for e) is in satisfactory agreement with experiment (see below).

cannot yet be evaluated and therefore (4) cannot be used for quantitative determination of the atomic magnetic moments.

In view of this, it makes no sense in practice to attempt to formulate semi-empirical relations for the magnetic parameters in terms of crystal-structure and electron-structure parameters of the metals, introduced in the first and this section. It is desirable here to be guided by the suggested analogy with Eq. (4) of Vonsovskiĭ-Vlasov for m and their relations for other magnetic parameters

By way of such a relation for ϵ (in the approximation of non-conducting ferromagnetic lattice: $J_s = 0$), we propose the following:

$$\epsilon = n_s \left\{ 1 + 0.15 \left[\frac{1}{e} \left(1 + \frac{1}{\beta\gamma} \right) - 4 \right] \right\}. \quad (5)$$

By adding the difference $N_d - n_s$ to (5), we find a relation for m , analogous to (4). Here β characterizes the orientation of the s -electron spin relative to the unpaired d electrons of the atoms: when $n_d \geq 5$ we have $\beta = -1$ (antiparallel orientation), and when $n_d < 5$ we have $\beta = 1$. According to van Vleck, the spin of the electron temporarily "arriving" on the cation from the anion (during the process of indirect exchange in FeO or MnO)

is also oriented with respect to the cation. For Cu, Ni, Co, Fe, and Mn the first condition ($\beta = -1$) is satisfied, while $\beta = +1$ for Cr, V, etc. The form of γ depends on the class of the metal: $\gamma^{(1)} = N_d - n_s - \Delta$, $\gamma^{(2)} = N_d - n_s + \Delta$, where the superscript denotes the class of the metal, on which the sign of Δ depends (the sign as the same as that of $r_1 - R$, which, by definition, is negative for class 1 and positive for class 2); Δ is calculated from (3).

We note that the first term in the square brackets of (5) is similar to Vonsovskii's equation¹⁶ for the s-d exchange energy of the s electron:

$$E_{sd} = -\frac{1}{2}A(\xi)[1 + (\eta\mu)],$$

where η is the vector of the spin of the s electron ($\eta = \pm 1$), μ is the average magnetic moment of the d electrons per atom, $A(\xi)$ is the exchange integral between an s electron with quasi-momentum ξ and one (nearest) d electron. We see that a) μ has the same meaning and same numerical values as β in Eq. (5), b) the first term in the square brackets of (5), like A, is also referred to one magnetic electron (the expression in the round brackets is divided by e), and c) in the approximation of strongly-bound electrons, A depends on the number n of the nearest neighbors of the atom in the lattice. But Δ also contains n, and contains, furthermore, the effective interatomic distance, on which J must naturally depend. The coefficient $\frac{1}{2}$ in the expression for E_{sd} also enters into Δ , since $0.642 \approx 2^{1/3}/2$. Thus, not only the fact that the first term in the square brackets of (5) is located in the place occupied by the exchange-integral ratio J_0/J in Eq. (4), but also the considerations listed above give rise to the thought that this term is connected with the integral of the s-d exchange in the lattice. In view of this, the plus sign in front of this term (for the ferromagnetic state of pure ferromagnetic metals) must be replaced by a minus sign in the case of transition metals that are not ferromagnetic in pure form (Mn and Cr), but play the role of ferromagnetic metals in many alloys (cf. below and reference 16, p. 192).

A similar change in sign should be made also when going from the ferromagnetic state of pure ferromagnetic metals to the paramagnetic state.

We have seen that in calculating Δ from (3) for Ni (A1) and Co (A3), only the nearest neighbors of the atom are considered, and for Fe (A2) the following neighbors are also considered. The nearest neighbors (-) and those following (+) in a type A2 lattice correspond, apparently, to exchange integrals with signs opposite to those indicated in the parentheses. In fact, it was indeed this circumstance that the

French authors (Neel, Fallot, and others) had in mind when they assumed that not the nearest neighbors of the Fe atom, but those following, participate in ferromagnetism. From our point of view, as shown above, both types of neighbors play a role in the spontaneous magnetization of a metal with a lattice of type A2. If we confine ourselves to the nearest neighbors (Δ_0) in a lattice of type A2 (see below) the sign of the exchange integral [and with it the sign of the first term in the square brackets of (5)] must be reversed (compared with the sign that corresponds to the case when both types of neighbors are considered). Let us cite several examples: 1) For Fe (as well as Co and Ni) in the paramagnetic state, it would be necessary to take the minus sign in the place indicated in Eq. (5) (instead of the plus sign for the ferromagnetic state); but the transition of Fe into the paramagnetic state differs from the analogous transition for Co and Ni in that in the case of Fe it is still necessary here to neglect the neighbors following the nearest ones (which are considered, as shown, in the ferromagnetic state). This causes another reversal of the sign (- into +), leaving the initial + sign in the place indicated in Eq. (5). 2) The alloy MnCu₂Al also has an A2 type lattice. In view of the fact that its ferromagnetism is due to Mn, then according to the foregoing, the sign in (5) should be minus; but for this alloy, as for other Geisler alloys, it is necessary to adhere to the nearest-neighbor approximation (see below), and consequently the initial + sign is retained in Eq. (5). 3) In weak Fe-Cr and Co-Cr solid solutions the Cr is paramagnetic and has the same lattices as the solvents - A2 and A3 respectively. Therefore, in the nearest-neighbor approximation and at a concentration close to zero, the spin of its s electron should have antiparallel orientations (-1 for Fe-Cr and +1 for Co-Cr, as confirmed experimentally,⁹ see reference 2).

Let us proceed to apply (5) to particular cases.

(a) Pure ferromagnetic metals. Considering the foregoing, we can rewrite (5) for pure ferromagnetic metals in the following form:

$$m^{(1)} = N_d + 0.15 n_s \left[\frac{(N_d - n_s - \Delta) - 1}{(N_d - n_s)(N_d - n_s - \Delta)} - 4 \right], \quad (6)$$

$$m^{(2)} = N_d + 0.15 n_s \left[\frac{(N_d - n_s + \Delta) - 1}{(N_d - n_s + \Delta)} - 4 \right]. \quad (7)$$

Δ is calculated from (3), and the initial data for this calculations are listed in Table I. Inserting the numerical values into (6) and (7) we obtain: $m^{(1)} = 2.20$ for Fe and 1.69 for Co (reference

16 gives 2.21₇ and 1.71 respectively); $m^{(2)} = 0.60$ for Ni (0.60₅ in reference 16); the values of reference 16 are experimental. If we confine ourselves to the nearest neighbors for Fe, i.e., we put $\Delta_0 = 1.31$ in (6) (instead of $\Delta = 1.80$), we get $m = 2.73$; the latter differs from the moment of the neighboring Co ($m = 1.7$) by unity. The reason why the values of the moments of neighboring elements of class 1 (of which one has an A2 lattice and the other a different one) do not differ by unity (whereas their atomic numbers differ by unity) is, according to (6), that the neighbors following the nearest ones also participate in the spontaneous magnetization of a metal with lattice A2.

(b) Ferromagnetic ordered alloys. We find that (6) and (7) can be used to calculate also the individual magnetic moments of the components of the foregoing alloys. Let us consider those investigated by neutron-diffraction,^{9,10} where it is possible to determine experimentally the difference in the aforementioned moments, and the individual moments can be evaluated from the results of saturation magnetization measurements.

The alloy FeCo has an A2 lattice (like Fe), which can be mentally subdivided into two simple cubic sublattices, one occupied by the iron atoms and the other by the cobalt. In each of the sublattices, an atom of a given kind is surrounded by six nearest neighbors of the same kind, at a distance $r_1 = a = 2.85 \text{ \AA}$.¹⁷ Since the condition $r_1 > R$ is satisfied for both components ($R_{\text{Co}} = 2.54 \text{ \AA}$, $R_{\text{Fe}} = 2.73 \text{ \AA}$), they are metals of class 2 (while pure Co and Fe are of class 1) and consequently, Eq. (7) is applicable to both. Inserting the numerical values into (3) we find $\Delta_{\text{Co}} = 1.19$, $\Delta_{\text{Fe}} = 0.46$. From Eq. (7) we obtain $m^{(2)} = 2.98$ and 1.96 for Fe and Co respectively (experiment⁸ yields 2.80 and 1.98 respectively).

The alloy Ni₃Fe has an A1 lattice (like Ni). The Ni atoms are located in the centers of the faces, while the Fe atoms are at the corners of the elementary cell. The atom Ni [2] is surrounded by eight nearest-neighbor nickel atoms at a distance $r_1 = 2.508 \text{ \AA}$, while Fe [2] is surrounded by six nearest-neighbor iron atoms at a distance $r_1 = a = 3.546 \text{ \AA}$;⁸ the class of the metal is indicated in the square brackets. According to Eq. (3), $\Delta = 3.13$ for Fe and 0.51 for Ni, and according to (7) $m^{(2)}$ is 3.04 and 0.51 for Fe and Ni respectively (experiment⁹ yields 2.97 ± 0.15 and 0.62 ± 0.05 respectively). Here and in what follows, the constant R for the component is the same as for the pure metal, and is calculated from (1) and (2).

The alloy Ni₃Mn has the same lattice and the

same arrangement of the atoms as the Ni₃Fe, except that manganese replaces the iron. Here $r_1 = 2.543 \text{ \AA}$ and $R = 2.408 \text{ \AA}$ for Ni [2]; $r_1 = a = 3.596 \text{ \AA}$ ¹⁹ and $R = 2.863$ for Mn [2]. From (3) we get $\Delta = 2.82$ for Mn and 0.69 for Ni. Inserting the numerical values in (7) we get $m^{(2)} = 0.67$ (experiment:⁹ 0.30 ± 0.05) for nickel. As to Mn, which is not ferromagnetic in pure form, in virtue of the previous statements concerning similar elements, we tentatively place a plus sign in front of the first term in the square brackets of (6) and (7), and then use the latter to calculate the moment. The same applies also to Cr (see below). To avoid repetition, we make use of (6) and (7) in similar cases, with the proviso that the indicated preliminary sign reversal has been made. According to (7) we have for manganese $m^{(2)} = 3.55$ and $m_{\text{Mn}} - m_{\text{Ni}} = 2.88$ (experiment:⁹ 3.18 ± 0.25 and 2.88 ± 0.20 respectively).

The calculated and experimental values are in satisfactory agreement in the case of the first two alloys. For the third alloy, such an agreement is found only for the difference in the moments of the components (we recall that only the difference is obtainable directly by neutron-diffraction), but the values of the moments themselves are greatly divergent. The calculated value of the moment for Mn (3.55) is practically the same as is frequently obtained experimentally (see below). The same can be said about the moment of nickel (0.67). On the other hand, the experimental value of the moment of nickel (0.30) is unreasonably small. We note also that in the calculation of the moments of the components we did not take into account the interaction with neighbors of different kind (say Co-Fe).

(c) Ferromagnetic chemical compounds with structure of the NiAs type. The compounds MnAs, MnSb, MnBi, CrSb, and CrTe contain only one transition element (Mn or Cr), which is responsible for their ferromagnetism. The atom of this element has two nearest neighbors at a distance r_1 and six following neighbors of the same kind at a distance $r_2 = a$ (a is the lattice parameter). For Mn in all the foregoing compounds, $N_d = 5$, and $n_s = 2$, while $N_d = 4$ and $n_s = 2$ for Cr.

In the compound MnAs, Mn [1] belongs to class 1 (in view of the fact that $r_1 = 2.84 \text{ \AA} < R = 2.86 \text{ \AA}$; $a = 3.71 \text{ \AA}$ ²⁰). According to (3), $\Delta = 3.30$, and according to (6) $m^{(1)} = 3.37$ (experiment²⁰ yields 3.40).

In MnSb, we have $r_1 = 2.89 \text{ \AA}$ for Mn [2] ($R = 2.86 \text{ \AA}$; $a = 4.12 \text{ \AA}$ ²⁰). According to (3) $\Delta = 4.89$, and according to (7) $m^{(2)} = 3.55$ (experiment²⁰ yields 3.53).

In MnBi we have $r_1 = 3.06 \text{ \AA}$ for Mn [2] ($R =$

2.86 Å, $a = 4.30 \text{ Å}^{20}$). According to (3) $\Delta = 5.80$ and according to (7) $m^{(2)} = 3.53$ (experiment²⁰ yields 3.52).

In CrSb we have $r_1 = 2.726 \text{ Å}$ for Cr [1] ($R = 3.058 \text{ Å}$; $a = 4.127 \text{ Å}^{10}$). From (3), $\Delta = 4.54$. In view of what has been said above regarding crystalline chromium (p. 867) we find that we can calculate its moment from Eqs. (6) and (7), except that a plus sign must be placed in front of the 1 in the numerators and, as before, a minus sign must precede the terms in the square brackets, as is the case for all transition elements which are non-ferromagnetic in pure form but ferromagnetic when alloyed. From (6), $m^{(1)} = 2.71$ (experiment¹⁰ — 2.7 ± 0.2).

In CrTe we have $r_1 = 3.105 \text{ Å}$ for Cr [2] ($R = 3.058 \text{ Å}$; $a = 3.981 \text{ Å}^{21}$). From (3), $\Delta = 3.61$ and from (7) $m^{(2)} = 2.45$ (experiment²¹ — 2.40).

(d) Ferromagnetic Geisler alloys MnCu_2Al , MnCu_2Sn , and MnCu_2In . In these alloys Mn [2] belongs to class 2 (since the distances between the nearest atoms of Mn, amounting to $r_1 = 4.17$, 4.35, and 4.39 Å respectively,²² are greater than $R = 2.86 \text{ Å}$). Each Mn atom is surrounded by twelve nearest atoms of the same kind. According to (3) $\Delta = 10.06$, 11.47, and 11.78 respectively. In view of statements made on p. 867, we obtain from (7) $m^{(2)} = 4.07$ (experiment²³ — 4.10).

(e) Ferromagnetic weak solid solutions. By way of an example, we consider the system Fe-Me with A2 lattice, where $\text{Me} = \text{V}, \text{Cr}, \alpha\text{-Mn}, \text{Co},$ and Ni . For these we have, at 100 atomic percent of Me, $m_{\text{Me}} = 1 + \beta [(N_d - n_s)_{\text{Me}} - 0.642 \times 6(a - R_{\text{Me}})] + 0.642 \times 8(R_{\text{Fe}} - R_{\text{Me}})$, where the difference $a - R_{\text{Me}}$ is found from the diagram. For A2 lattices the difference $N_d - n_s$ equals the number of electrons actually contained in the d shell of the crystal atom. Assuming that $N_d - N_s = 0$ for the antiferromagnetic Cr and $\alpha\text{-Mn}$ and unity for V, then $m_{\text{Me}} = 0$ (0) for V and Cr, 0.2(0.2) for Mn, 1 (1.2) for Ni, and 3.1 (3.4) for Co; the parentheses contain the experimental values. These results do not agree with the premises of Lomer and Marschall,⁸ who assume that the filling of the atomic shells begins with Cr, that Mn has one d electron, and V has none.

Paramagnetic atomic magnetic moment and Curie constant. The atomic magnetic moment of ferromagnetic metals in the paramagnetic state is $m_p = \sqrt{\sigma(\sigma+2)}$, where σ is the number of paramagnetic electrons (participating in the paramagnetism) per atom. We shall show that this number can be calculated from relations analogous to (6) and (7). Assume that only the nearest neighbors of the atom (Δ_0) contribute to the moment

m_p of all transition metals. Nothing is different in this respect for metals having lattices other than A2 (for example Co and Ni), since only the nearest neighbors participate even in their spontaneous magnetization. However, this assumption changes matters substantially for metals with A2 lattices (say Fe), for as we have seen even the atoms following the nearest neighbors contribute to their spontaneous magnetization, but here (in the case of paramagnetism) these are neglected. In the case of iron, in particular, this necessitates a plus sign in front of the square brackets in (5), cf. p. 867, while in the case of Co and Ni a minus sign is necessary (instead of the plus for the ferromagnetic state). Next, for example, for pure ferromagnetic metals, the denominators of (6) and (7) contain the integral parts [$e^{(1)} = N_d - n_s$ or $e^{(2)} = 1$] and the fractional parts [$\gamma^{(1)} = N_d - n_s - \Delta$ or $\gamma^{(2)} = N_d - n_s + \Delta$]* of the number of ferromagnetic electrons, m . Assume that the foregoing integral parts are retained also for the paramagnetic state. As to the fractional parts, it is obvious that they are quite different; they must now be replaced by the fractional parts of the numbers of electrons that do not participate in the ferromagnetism. We assume that the latter equal $n_s - \gamma^{(1)}$ or $n_s - \gamma^{(2)}$.

Finally, the signs in front of γ_0 and 1 in the sought relations for m_p should be the same as in (6) and (7), for they are determined by the class of metal and by the orientation of the s - electron spin (both of which remain unchanged).

Considering all the foregoing, we find

$$\sigma^{(1)} = N_d + 0.15n_s \left[-\frac{n_s - N_d - \Delta_0 - 1}{(N_d - n_s)(2n_s - N_d + \Delta_0)} - 4 \right], \quad (8)$$

$$\sigma^{(2)} = N_d + 0.15n_s \left[-\frac{n_s - N_d + \Delta_0 - 1}{2n_s - N_d - \Delta_0} - 4 \right]. \quad (9)$$

Inserting the numerical values in (8) and (9) we get: $\sigma^{(1)} = 2.34$ and $m_p^{(1)} = 3.19$ (experiment²⁴ — 3.20) for Co; $\sigma^{(1)} = 2.31$ and $m_p^{(1)} = 3.18$ (experiment²⁴ — 3.20) for Fe; $\sigma^{(2)} = 0.89$ and $m_p^{(2)} = 1.60$ (experiment²⁴ — 1.60) for Ni.

Let us find the same quantities for MnAs and MnSb (the latter are chosen because we know their Curie constants C_0 per gram atom, which are proportional to $m_p^{(2)}$). $\Delta_0 \approx 0$ for both com-

*For pure ferromagnetic metals, Eq. (5) and the relations written for $\gamma^{(1)}$ and $\gamma^{(2)}$ yield practically the same values; (5) is the more general. It is seen from this that ε (or, what is the same, $\gamma^{(1)}$ or $\gamma^{(2)}$) is a fraction of n_s ; in view of this, it is assumed that the number of electrons not participating in the ferromagnetism is the remainder of n_s , i.e., $n_s - \varepsilon$ or $n_s - \gamma$.

pounds. From (8) we have $\sigma^{(1)} = 3.61$ and $(m_p^{(1)})^2 = 20.24$, $\sigma^{(2)} = 3.24$ and $(m_p^{(2)})^2 = 17$ for MnAs and MnSb respectively.

Inserting the numerical values into the following relation

$$C_0 = LM_B^2 m_p^2 / 3k \quad (10)$$

(L is the number of atoms per gram-atom and k is Boltzmann's constant), we obtain $C_0 = 0.325$ (0.322^{25}), 1.267 (1.228^{25}), 1.250 (1.265^{25}), 2.565 (2.594^{20}), and 2.110 (2.085^{20}) for Ni, Co, Fe, MnAs, and MnSb, respectively. The parentheses contain the experimental values and the references).

$$\Theta^{(1)} = \frac{n(n-1)(1+N_d^2)}{1-0.15n_s(N_d-n_s-\Delta_0)\{4+[1-(N_d-n_s-\Delta_0)/(N_d-n_s-\Delta_0)]^2/nn_d\}}, \quad (12)$$

$$\Theta^{(2)} = \frac{n(n-1)(1+N_d^2)}{1-0.05n_s\Delta_0\{4+(1-\Delta_0)^2/nn_d\}} - nn_s(n_s+2)/3, \quad (13)$$

where n is the number of nearest neighbors. According to (12) and (13), $\Theta^{(1)} = 1041^\circ\text{K}$ (experiment²³ - 1043°K) for Fe and 1389°K (experi-

Curie Points

According to the theory of Vonsovskii and Vlasov, the ferromagnetic Curie point is

$$\Theta = \Theta_{dd} / [1 - 0.15 n_0 J (J_0/J - 4)^2 / b (1 - 2J_s/J) N], \quad (11)$$

where $\Theta_{dd} = b/2k$ is the Curie point produced by d-d exchange only, b is an exchange integral on the order of J, and n_0 and N are the numbers of s and d electrons per cubic centimeter. It is impossible to calculate Θ from (11). We propose in its stead the following semi-empirical relations:

ment²³ - 1393°K) for Co; $\Theta^{(2)} = 637^\circ\text{K}$ (631°K^{23}) for Ni.

The paramagnetic Curie point is

$$\Theta_p^{(1)} = \frac{n(n-1)(1+N_d^2)}{1-0.15n_s(2n_s-N_d+\Delta_0)\{4-[1-(2n_s-N_d+\Delta_0)/(2n_s-N_d+\Delta_0)]^2/nn_d\}}, \quad (14)$$

$$\Theta_p^{(2)} = \frac{n(n-1)(1+N_d^2)}{1-0.05n_s(2n_s-N_d-\Delta_0)\{4-[1-(2n_s-N_d-\Delta_0)/(2n_s-N_d-\Delta_0)]^2/nn_d\}} - nn_s(n_s+2)/3. \quad (15)$$

According to (14) and (15), $\Theta_p^{(1)} = 1116^\circ\text{K}$ (1101°K^{25}) for Fe and 1435°K ($1428-1403^\circ\text{K}^{25}$) for Co; $\Theta_p^{(2)} = 646^\circ\text{K}$ (650°K^{25}) for Ni.

Exchange Energy

The exchange energy equals

$$A^{(1)}/k = (N_d - n_s - \Delta_0) \Theta^{(1)} / (N_d - n_s)^2 \quad (16)$$

$$A^{(2)}/k = (1 - \Delta_0) \Theta^{(2)} - nn_s(n_s + 2) / 3. \quad (17)$$

According to (16) and (17), $A^{(1)}/k = 180$ (183^{26} , 207^{27}) for Fe and 1014 for Co; $A^{(2)}/k = 223$ (226^{26} , 220^{27}) for Ni.

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230

Vacuum Tubes (see Methods and Instruments)

Viscosity (see Liquids)

Wave Mechanics (see Quantum Mechanics)

Work Function (see Electrical Properties)

X-rays

Anomalous Heat Capacity and Nuclear Resonance in Crystalline Hydrogen in Connection with New Data

on Its Structure. S. S. Dukhin — 1054L.

Diffraction of X-rays by Polycrystalline Samples of Hydrogen Isotopes. V. S. Kogan, B. G. Lazarev, and R. F. Bulatova — 485.

Investigation of X-ray Spectra of Superconducting CuS.

I. B. Borovskii and I. A. Ovsyannikova — 1033L.

Optical Anisotropy of Atomic Nuclei. A. M. Baldin — 142.

ERRATA TO VOLUME 9

On page 868, column 1, item (e) should read:

(e). Ferromagnetic weak solid solutions. By way of an example, we consider the system Fe-Me with A2 lattice, where Me = Ti, V, Cr, Mn, Co, and Ni. For these the variation of the moment m with concentration c is

$$dm/dc = (Na)_{Me} \mp 0.642 \{ 8 (2.478 - R_{Me}) + 6 |2.861 - R_{Me}| \mp [8(2.478 - R_{Fe}) + 6(2.861 - R_{Fe})] \},$$

where the signs $-$ and $+$ pertain respectively to ferromagnetic and paramagnetic Me when in front of the curly brackets, and to metals of class 1 and 2 when in front of the square brackets. The first term and the square brackets are considered only for ferromagnetic Me. We then have $dm/dc = -3$ (-3.3) for Ti, -2.6 (-2.2) for V, -2.2 (-2.2) for Cr, -2 (-2) for Mn, 0.7 (0.6) for Ni, and 1.2 (1.2) for Co; the parentheses contain the experimental values.

ERRATA TO VOLUME 10

Page	Reads	Should Read
224, Ordinate of figure	10^{23}	10^{29}
228, Column 1, line 9 from top	3.6×10^{-2} mm/min	0.36 mm/min
228, Column 1, line 16 from top	0.5 mm/sec	0.05 mm/min
329, Third line of Eq. (23a)	$+ (1/4 \cosh r + \dots$	$+ 1/4 (\cosh r + \dots$
413, Table II, line 2 from bottom	$-0.0924 \pm$	$-1.0924 \pm$
413, Table II, line 3 from bottom	$+1.8730 \pm$	$+0.8370 \pm$
479, Fig. 7, right, 1st line	92 hr	9.2 hr
499, Second line of Eq. (1.8)	$+\tilde{k} \sin^2 \alpha / \omega_N^2 + \langle c^2 \tilde{k}^2 \dots$	$+\left(\tilde{k}/\omega_H\right)^2 \sin^2 \alpha \langle c^2 \tilde{k}^2 \dots$
648, Column 1, line 18 from top	18×80 mm	180×80 mm
804, First line of Eq. (17)	$-1/3 (\alpha_x^2 \alpha_y^2 + \dots$	$\dots - 3 (\alpha_x^2 \alpha_y^2 + \dots$
967, Column 1, line 11 from top	$\sigma(N', \pi) \approx 46(N', N')$	$\sigma(N', \pi) > \sigma(N', N')$
976, First line of Eq. (10)	$= \frac{e^2}{3r^2c^4}$	$= \frac{e^2}{3\hbar^2c^2}$
978, First line of Eq. (23)	$\left[\frac{(2\gamma^2 - 1)^2}{(\gamma^2 - 1) \sin^4(\theta/2)} \right]$	$\left[\frac{(2\gamma^2 - 1)^2}{(\gamma^2 - 1)^2 \sin^4(\theta/2)} \right]$