ON THE THEORY OF AMORPHOUS AND LIQUID FERROMAGNETS

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We start from a Heisenberg model without lattice periodicity and investigate $\chi(T)$, $\sigma(T)$, and T_C in the molecular field approximation. Exchange integrals, spins, and the molecular field fluctuate in consequence of structure fluctuations. We obtain a Curie-Weiss law with a slightly modified Curie temperature. The fluctuations of the exchange integral cause a decrease of $\sigma(T)$. If the mean square fluctuation of the exchange integral is larger than its mean value, ferromagnetism does not exist. From this condition it is obvious that with regard to the ion structure ferromagnetism can exist in liquids, too.

1. Introduction

In recent years the question was repeatedly discussed whether or not ferromagnetism can also exist in noncrystalline materials.

Thin amorphous films of Fe [1], Co−P [2], and Co−Au [3], produced by evaporation onto a cold substrate, have been investigated. Examinations of structure by electron diffraction have shown high diffuse rings, which are typical for a liquid structure. Ferromagnetic domains were made visible by Lorentz electron microscopy. Ferromagnetic resonance signals in thin amorphous Co−Au films were found by Elschner and Gärtner [4]. Measurements of spontaneous magnetization in amorphous Ni films by Tamura and Endo [5] yielded a reduction of the saturation magnetization and of the Curie temperature in comparison with the crystalline state. In a systematic manner Felsch [6] produced ferromagnetic amorphous Fe films by adding small quantities of Fe_2O_3, Si, or Ge during the evaporation process and investigated the coercive force and the saturation magnetization. More extensive samples (thickness $\approx$50 μ) produced by quenching the liquid phase with the composition $Pd_{68}Co_{12}Si_{20}$, $Pd_{75}Fe_5Si_{20}$ [7], and $Fe_{80}P_{12.5}C_{7.5}$ [8, 9] were investigated, too. Measurements of the bulk magnetization and of the hyperfine field by Mössbauer spectroscopy [9] yielded a typical ferromagnetic temperature dependence.

In the liquid state the static susceptibility χ of iron, cobalt, nickel, manganese, and of various alloys containing transition metals was measured. The temperature dependence

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of χ is not essentially different from that in the solid phase above the magnetic transition point [10 to 13]. Busch and Guentherodt [14] investigated a liquid Co−Au alloy near the eutectic composition and concluded that ferromagnetism existed. However, it is not clear at present whether or not this ferromagnetic behaviour originates from Co-clusters which have either remained from the melting process, as suggested by Wachtel and Kopp [15], or have been formed in small regions for a short time. This explanation of ferromagnetism is plausible, because the Curie temperature given in [14] is nearly equal to the Curie temperature for pure cobalt. On the other hand, for this alloy Nakagawa [16] has found a T_C far below the melting point, in agreement with [15].

The question whether or not ferromagnetism may exist in amorphous substances was theoretically studied first by Gubanov [17]. He started from a mean spatial arrangement of neighbouring spins described only by the radial distribution function $g(r)$. For an Ising model with distance-dependent exchange integral $I(r)$ he found within the so-called quasichemical approximation that a finite Curie temperature may exist. However, the influence of structure fluctuations is not considered in this paper. Conclusions regarding the micromagnetic behaviour of nonordered ferromagnets resulting from the lack of crystal anisotropy were arrived at by de Gennes and Pincus [18].

In the experimentally investigated amorphous substances one can exclude crystalline long-range order, but not with certainty the existence of short-range order regions. Mader and Nowick [3] stated 15–20 Å for the maximum size of these regions. Tsuei *et al.* [9] obtained liquid-like X-ray diffraction patterns and calculated a mean atomic distance of 2.6 Å with a mean deviation of 0.5 Å. Doubtlessly, crystalline order in small regions would influence the ferromagnetic behaviour and favour the formation of a ferromagnetic phase. However, neither crystalline long-range order nor short-range order is necessary for the existence of ferromagnetism, as is shown in [19] and will be demonstrated in the following.

In this paper in Section 2 a model describing amorphous and liquid ferromagnets is proposed. We start from the Heisenberg model. Contrary to the crystalline case, we must omit the lattice periodicity of the Hamiltonian. In the following, the molecular field approximation is used as the simplest ferromagnetic theory. The molecular field in this case changes stochastically. One gets the macroscopic magnetization by averaging with respect to the structure. Furthermore, two simple approximations making structure averaging practicable are considered. In Section 3 for $T > T_C$ a Curie–Weiss law results with a modified Curie temperature. The structure fluctuations decrease the reduced magnetization. A necessary condition for the existence of a ferromagnetic phase in amorphous and liquid materials has been found. In Section 4 small fluctuations of the exchange integral are considered more exactly by means of an iteration method. In Section 5 some further problems and questions are discussed.

2. Model

We consider a system of spins localized on the atomic trunks. Because of the lack of lattice periodicity the Hamiltonian in the Heisenberg model

$$\mathscr{H} = \sum_{i \neq j} I_{ij} \hat{S}_i \hat{S}_j + \sum_i \mu_B g_i \hat{S}_i^z H \tag{1}$$

is not translation invariant. $\hat{S}_i$ and $\hat{S}_j^z$ are the operators of the i-th spin and its z-component, respectively, I_{ij} are the exchange integrals, g_i is the Landé splitting factor, μ_B the Bohr magneton, and H the external field in z-direction. In (1) it is assumed that the exchange integrals I_{ij} only depend on the positions of the two interacting spins, and the spin operator $\hat{S}_i$ only depend on its position. In the general case they also depend on the positions of the other atoms in the next neighbourhood of the i-th (j-th) atoms, $i.e.$ on the concrete structure in the next neighbourhood[1]. But for simplicity we have assumed in (1) that the exchange integrals and the spin operator are functions on the mean structure of the next neighbourhood only. We remember that also for the calculation of electron and phonon spectra in amorphous matter one has to make a reduction to effective two-body interactions in the same sense. This procedure is allowed for small structure fluctuations.

Because of the lack of lattice periodicity a correct treatment of the Heisenberg model is impossible. Therefore, further approximations are necessary. In the molecular field approximation, which describes in a qualitatively correct manner the essential feature of ferromagnetism, the spin operators $\hat{S}_j$ are replaced by their time mean values $\overline{S}_j^z$. So a decoupling of the spin operators is obtained and (1) passes into

$$\mathcal{H} = \sum_i \mu_B g_i \hat{S}_i^z (H + H_{W_i}) \tag{2}$$

with

$$H_{W_i} = \frac{1}{\mu_B g_i} \sum_{j(\neq i)} I_{ij} \overline{S}_j^z. \tag{3}$$

Consequently, every spin i is in its molecular field H_{W_i}, according to the individual neighbourhood. For the same reason the spin mean value is different for every atom and depends
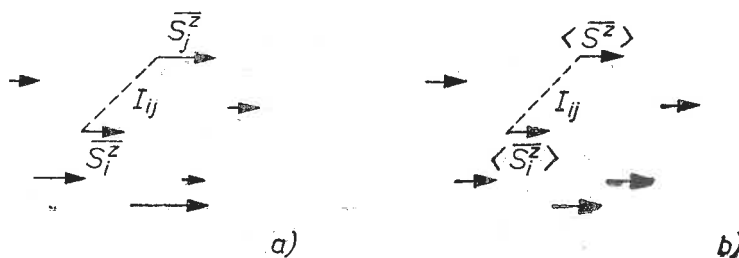

Fig. 1. Representation of the spin arrangement. a) according to approximation (3); b) according to approximation (4)

on its index (Fig. 1a). For further simplification the spin mean values $\overline{S}_j^z$ may be substituted approximately by their spatial mean value $\langle \overline{S}^z \rangle$ Fig. 1b):

$$H_{W_i} \rightarrow \frac{1}{\mu_B g_i} \sum_{j(\neq i)} I_{ij} \langle \overline{S}^z \rangle. \tag{4}$$

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[1] In disordered alloys (with lattice structure), $e.g.$ in Fe_3Al, the spin S_{Fe} depends on the concrete number of Fe and Al atoms in the next neighbourhood.

Thus, a decoupling with respect to the spatial dependence of the spins is obtained. The procedure (4) corresponds to a repeated application of the molecular field approximation idea relative to the structure.

For a random but fixed array of atoms one gets for the time mean value of the spin i

$$\overline{S}_i^z = S_i B_{S_i}[\beta S_i \mu_B g_i (H + H_{W_i})]. \tag{5}$$

S_i is the total spin of the i-th atom, and B_{S_i} is the Brillouin function. In the approximation (3) the $\overline{S}_i^z$ depend on $\overline{S}_j^z$ which cause the molecular field H_{W_i}. Therefore, the relation (5) is a coupled transcendent equation system for all $\overline{S}_i^z$. Actually, the individual $\overline{S}_i^z$ do not interest us, but only the macroscopic magnetization. Therefore, one has to average over all atom configurations. For this end we sum (5) over all i and average with the distribution function $f_N(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N)$. We will abbreviate this procedure by $\langle ... \rangle$. It follows that

$$\langle \overline{S}^z \rangle = S \langle B_S[\beta S \mu_B g (H + H_{W_i})] \rangle. \tag{6}$$

With special assumptions the reduced magnetization $\sigma = \langle \overline{S}^z \rangle / S$ can be calculated from this equation. In (6) it was suggested that all atoms have the same total spin S and the same g-factor.

For the structure averaging one has to take into consideration that the I_{ij} and the $\overline{S}_j^z$ must be treated differently. Whereas the exchange integrals I_{ij} must be regarded as known functions of $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$, the $\overline{S}_j^z$ are unknown and really not only dependent on $\boldsymbol{r}_j$, but also on the position and the size of the neighbouring spins because of the exchange integrals I_{ij}.

This procedure is justified, if the spatial structure does not depend on the ferromagnetic state, *i.e.* if one can neglect magnetoelastic effects. In liquids one has to require additionally that the characteristic time for adjusting the spin order is small in comparison with the characteristic time for particle diffusion. In this case liquids can be treated as amorphous substances.

3. Simplest approximation for χ and σ

In this Section we use the approximation (4)[2]. For $T \gg T_C$ the argument of the Brillouin function in (5) is small and one gets

$$\overline{S}_i^z = \frac{S(S+1)}{3} \beta \left(\mu_B g H + \sum_{j(\neq i)} I_{ij} \langle \overline{S}^z \rangle \right). \tag{7}$$

After the structure averaging of (7) a Curie–Weiss law

$$\sigma = \frac{C}{T - T_C} H \text{ with } C = \frac{\mu_B g (S+1)}{3k}, \quad T_C = \frac{S(S+1)}{3k} N \langle I_{12} \rangle \tag{8}$$

follows analogously to the result of the molecular field approximation for crystalline ferromagnets. The only difference is the occurence of the mean exchange integral

$$\left\langle \sum_{j(\neq i)} I_{ij} \right\rangle \equiv N \langle I_{12} \rangle = 4\pi \frac{N}{V} \int dr \, r^2 \, g(r) \, I(r). \tag{9}$$

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[2] Indeed, only this approximation was used in [19].

It is assumed that $I_{ij} = I(\mathbf{r}_i - \mathbf{r}_j)$ and that the sample is homogeneous and isotropic. $g(r)$ is the radial distribution function.

The measurements of the susceptibility in liquid transition metals and alloys yield a good agreement with the Curie–Weiss law [10 to 13]. Insignificant deviations from it can be explained by weak temperature dependence of the radial distribution function.

Now, for $T < T_C$ we deal with the small fluctuations of the exchange integral about the mean value (9). Starting from (5) we get for $H \to 0$

$$\bar{S}_i^z = S B_S(\beta S \sum_{j(\neq i)} I_{ij} \langle \overline{S^z} \rangle). \tag{10}$$

In the nonordered case the term $\sum_j I_{ij}$ depends on i. Therefore, it is useful to write

$$\sum_{j(\neq i)} I_{ij} = N \langle I_{12} \rangle + \sum_{j(\neq i)} \Delta I_{ij}. \tag{11}$$

The second term originates from the structure fluctuations. Now we expand (10) into $\sum \Delta I_{ij}$ terms neglecting higher order terms. After structure averaging we get

$$\sigma = B_S(x) + \frac{1}{2} B_S''(x) x^2 \Delta^2 \quad \text{with} \quad x = \frac{3S}{S+1} \frac{\sigma}{\tau} \tag{12}$$

$$\text{and } \Delta^2 = \frac{\langle (\Sigma_j \Delta I_{ij})(\Sigma_k \Delta I_{ik}) \rangle}{\langle \Sigma_j I_{ij} \rangle^2} \equiv \frac{\langle \Delta I_{12} \Delta I_{13} \rangle}{\langle I_{12} \rangle^2}, \quad \tau = \frac{T}{T_C}.$$

Apart from the Curie temperature T_C, Δ^2 here occurs as a new parameter which represents a measure for the mean square fluctuation of the exchange integral due to structure fluctuations. Because $B_S''(x) < 0$ for $x > 0$, it follows from (12) that the fluctuations of the exchange integral cause a decrease of reduced magnetization.

For consideration of any structure fluctuations we write (6) in the form

$$\sigma = \left\langle B_S \left[x \left(1 + \frac{\Sigma_j \Delta I_{ij}}{N \langle I_{12} \rangle} \right) \right] \right\rangle \tag{13}$$

and expand into fluctuation terms. In [19] the higher products were approximated in the following way

$$\langle \Delta I_{12} \Delta I_{13} \dots \Delta I_{1(n+1)} \rangle = \begin{cases} 0 & \text{for } n \text{ odd} \\ \langle \Delta I_{12} \Delta I_{13} \rangle^{n/2} & \text{even.} \end{cases} \tag{14}$$

After summation we get the simple relation

$$\sigma = \frac{1}{2} \{ B_S[x(1+\Delta)] + B_S[x(1-\Delta)] \}. \tag{15}$$

This equation was discussed in [19]. It follows that with increasing fluctuations Δ the magnetization decreases and for $\Delta > 1$ vanishes for all T. These results can be interpreted as follows: Because of the random array of the spin-carrying atoms there is a decrease of the exchange energy in small regions. Thus, it is possible that some spins can be ousted out of the favoured

direction easier. Thus, the effect of the increase of structure fluctuations (at fixed T) is analogous to the effect of thermal fluctuations (at $\Delta = 0$). However, differences also exist. At increasing structure fluctuations the sign of the exchange interaction will become negative for more and more spins. It follows that the number of spins adjusting stochastically in opposition to the favoured direction becomes larger. If the fluctuations exceed a critical value, the magnetic long-range order breaks down.

For examination of the dependence of our result on the special assumption (14), we replace it by

$$\langle \Delta I_{12} \Delta I_{13} \ldots \Delta I_{1\,(n+1)} \rangle = \begin{cases} 0 & \text{odd} \\ \dfrac{n\,(n-1)}{2} \langle \Delta I_{12} \Delta I_{13} \rangle^{n/2} & \text{for } n \quad \text{even} \end{cases} \tag{16}$$

providing the higher products with more weight. Then the relation for σ becomes

$$\sigma = B_S(x) + \frac{1}{2}\, x^2 \Delta^2 \{ B_S''[x(1+\Delta)] + B_S''[x(1-\Delta)] \}. \tag{17}$$

Because $B_S''(x) < 0$, σ becomes again smaller for increasing Δ. For $\Delta > 1$, σ in (17) can become bigger than unity because of $B_S''(x) = -B_S''(-x)$. In this case only, $\sigma = 0$ for all T remains as a reasonable solution of (17) as before. Therefore, we may generalize that a ferromagnetic phase can only exist on condition that

$$\langle \Delta I_{12} \Delta I_{13} \rangle^{1/2} \lesssim \langle I_{12} \rangle. \tag{18}$$

Approximately, one can assume that $N^2 \langle \Delta I_{12} \Delta I_{13} \rangle \sim \langle (\Delta z)^2 \rangle I^2$ and $N^2 \langle I_{12} \rangle^2 \sim \langle z \rangle^2 I^2$, with z as the number of the nearest neighbours. In [20]

$$\frac{\langle (\Delta z)^2 \rangle^{1/2}}{\langle z \rangle} \approx 0.1 \ldots 0.3 \tag{19}$$

is given for liquid metals. Thus, the ionic structure of liquid metals allows the existence of a ferromagnetic phase. Occurring globula (crystal-like structure in small regions) would favour ferromagnetism additionally. However, the melting point T_m must lie below the Curie point. To achieve this, one must search for suitable alloys. Up to now it seems that forcible arguments for or against the possibility of guaranteeing the condition $T_m < T_C$ do not exist.

With knowledge of the distribution function for the fluctuations of the exchange intgral $F(\delta I)$ with $\delta I \equiv \sum_j \Delta I_{ij}$ we could get σ by averaging:

$$\sigma = \int d(\delta I) F(\delta I) B_S[\beta S(\langle I \rangle + \delta I) \langle \bar{S}^z \rangle]. \tag{20}$$

However, it is not clear what distribution function must be chosen. Nevertheless, one can conclude from the curvature of the Brillouin function without knowledge of F that the fluctuations of the exchange integral always yield a decrease of magnetization.

Measurements of the reduced magnetization of amorphous $Fe_{80}P_{12.5}C_{7.5}$ as a function of reduced temperature by Tsuei et al. [9] qualitatively agree with our results (15) and (17),

respectively, if we compare them with the curves for pure crystalline Fe. Also, numerical calculations of a one-dimensional Ising model with nearest neighbour interaction show a decrease of the magnetization with increasing fluctuation of the exchange integral [21].

4. A more accurate consideration of weak structure fluctuations

Now we start from the equation (5) with the molecular field (3). Contrary to the previous Section, we use here the exact mean value of the molecular field

$$\frac{1}{\mu_B g} \langle H_W \rangle = \left\langle \sum_{j(\neq i)} I_{ij} \overline{S_j^z} \right\rangle = N(\langle I_{12} \rangle + \langle \alpha \rangle) \langle \overline{S^z} \rangle$$

where

$$N \langle \alpha \rangle \langle \overline{S^z} \rangle \equiv \langle \sum_{j(\neq i)} \Delta I_{ij} \Delta \overline{S_j^z} \rangle. \tag{21}$$

With the reasonable assumption that the total mean molecular field is proportional to the mean spin $\langle \overline{S^z} \rangle$, the macroscopic spontaneous magnetization is sure to vanish, if the mean molecular field tends to zero. Because of (21), the Curie temperature (8) must be replaced by

$$T_C = \frac{S(S+1)}{3k} N(\langle I_{12} \rangle + \langle \alpha \rangle). \tag{22}$$

For weak structure fluctuations we apply an iteration procedure. The starting point is

$$\overline{S_i^{z(0)}} = S B_S (\beta S \langle \sum_{j(\neq i)} I_{ij} \overline{S_j^z} \rangle). \tag{23}$$

Now we expand into $\Delta H_{W_i} \sim \sum_j I_{ij} \overline{S_j^z} - \langle \sum_j I_{ij} \overline{S_j^z} \rangle$. If we replace $\overline{S_j^z}$ in the correction term by the value of next lower order, we get, for instance in the first approximation,

$$\overline{S_i^{z(1)}} = S(B_S + B_S' \beta S \langle \overline{S^z} \rangle \sum_j \Delta I_{ij}). \tag{24}$$
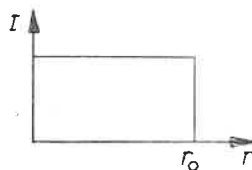

Fig. 2. Example of a simple r-dependence of the exchange integral for the discussion of the influence of structure fluctuations

The iteration procedure, to second order with regard to the fluctuation term, yields

$$T_C^{(2)} = \frac{S(S+1)}{3k} N \langle I_{12} \rangle (1 + \Delta^2). \tag{25}$$

for the Curie temperature, and a magnetization which is not essentially different from (12).

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5. Summary of results and problems

1. For the existence of a ferromagnetic phase neither long-range nor short-range crystalline order is necessary. Considering a special r-dependence of the exchange integral, according to Fig. 2, it is obvious that the ferromagnetic behaviour depends on the number of atoms between $r = 0 \ldots r_0$ only and not on the arrangement in this region.

2. In general, structure fluctuations yield a decrease of the spontaneous magnetization in comparison with the ordered case. Contrary to amorphous ferromagnets, in crystalline ones the atoms at equivalent lattice points have the same neighbours and, therefore, the same molecular field ($\sum_j \Delta I_{ij}$ is identical to 0). This means that the crystalline order favours the occurence of ferromagnetism, although it is not a necessary condition.

3. A critical value of the fluctuations, approximately given by the relation $\langle \Delta I_{12} \Delta I_{13} \rangle \lessgtr \langle I_{12} \rangle^2$, does exist. For higher fluctuations of the exchange integral a ferromagnetic phase is impossible.

4. In the approximations used here the molecular field fluctuations do not influence the Curie point; however, an amorphous ferromagnet can have a higher Curie point than in the crystalline state, since $N\langle I_{12} \rangle (1 + \Delta^2) > ZI$ is possible. The influence of structure fluctuations on the Curie temperature would presumably prove to be stronger in a more precise theory which takes into account magnetic short-range order.

5. In a more precise theory we must distinguish whether or not all I_{ij} are positive. In the first case $\sigma \rightarrow 1$ follows for $T \rightarrow 0$, whereas in the second one some spins would be arranged opposite to the mean molecular field also for $T \rightarrow 0$, and σ will be smaller than 1. Then in a stochastic way small "antiferromagnetic regions" will occur. It must be possible, to reveal them by a strong external magnetic field. We suppose that the measurements of amorphous Ni films by Tamura and Endo [5] can be explained in this way. However, the approximations in Section 3 are too rough for describing such effects.

6. An interesting question results in the case when $N\langle I_{12} \rangle < 0$. Then, in our opinion, a kind of amorphous antiferromagnetism can exist for not too high structure fluctuations. The $\chi^{-1}(T)$ curves of liquid manganese [13] in the paramagnetic region point to a mean negative exchange coupling. However, from this alone one cannot conclude about the existence of an antiferromagnetic phase in amorphous or liquid materials.

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