

# On the temperature dependence of the magnetization of ferromagnetic metallic glasses

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The temperature dependence of the magnetization of ferromagnetic metallic glasses is analyzed in the model of band magnetism. It is shown that this approach can eliminate two observed anomalies: a) the disagreement between the spin-wave dispersion parameter  $A = \omega/k^2$  and the coefficient  $D$  in the Bloch three-halves law; b) the softening of the spin wave (a significant decrease in the parameter  $A$  in comparison with the crystalline case). The disagreement between the parameters  $A$  and  $D$  is interpreted as resulting from neglect of the contribution of the Fermi excitations typical of band magnetism in the analysis of the experiment. The softening of the spin wave here is seen as a consequence of the fusion of the subbands of the  $3d$  band in the electron energy distribution of metallic glasses. The model could be checked by direct observation of the shape of the  $3d$  band in metallic glasses.

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## 1. METALLIC GLASSES AS BAND FERROMAGNETS

The study of ferromagnetic glasses is currently of great interest both in connection with important technical applications and also in regard to fundamental physical questions about the glassy state of matter. Despite the large number of studies devoted to noncrystalline ferromagnets (see the review in Ref. 1), there is still much to be explained in the behavior of such materials. The unexplained anomalies of ferromagnetic glasses include the temperature dependence of their spontaneous magnetization. Let us recall first of all how the spontaneous magnetization of ferromagnets with localized magnetic electrons (dielectrics,  $4f$  metals) depends on the temperature. In materials of this kind the principal mechanism for the decrease of the magnetization with increasing temperature is the excitation of thermal magnons. For  $T \ll T_c$  ( $T_c$  is the Curie temperature) the contribution of the thermal magnons to the magnetization  $M(T)$  contains terms proportional to  $T^{3/2}$ ,  $T^{5/2}$ , ..., and therefore

$$M(T) = M(0) \{1 - DT^{3/2} - D_1 T^{5/2} - \dots\}. \quad (1)$$

The first term on the right-hand side of this relation gives the familiar Bloch three-halves law. Here the parameter  $D$  is related to the coefficient  $A$  in the spin-wave dispersion relation by

$$D = \frac{2.612\gamma\mu_B}{M(0)} (4\pi A)^{-3/2} \quad (2)$$

( $\gamma$  is the spectroscopic splitting factor, and  $\mu_B$  is the Bohr magneton).

In ferromagnets with collectivized magnetic electrons (band ferromagnets) there is another mechanism in addition to the excitation of thermal magnons that leads to the decrease of the spontaneous magnetization with increasing temperature—the thermal excitation of the collectivized electrons. The contribution of these (so-called “Stoner”) Fermi excitations leads to a decrease in  $M(T)$  according to the law<sup>2</sup>

$$M(T) = M(0) (1 - GT^2)^{1/2},$$

where  $G$  is a constant characterizing the particular ferromagnet. Thus the first terms in the expansion of  $M(T)$  in powers of  $T$  in these materials are of the form

$$M(T) = M(0) \{1 - DT^{3/2} - \frac{1}{2}GT^2\}. \quad (3)$$

It is known<sup>3</sup> that in crystalline  $3d$  metals the Bloch term  $DT^{3/2}$  plays a role only at very low temperatures; over a wide range of temperatures (all the way up to  $T \approx 0.5T_c$ ) the magnetization behaves according to the law typical of band ferromagnets:

$$M(T) = M(0) (1 - GT^2)^{1/2}.$$

In other words, for crystalline  $3d$  metals the temperature dependence of the magnetization is described by formula (3) rather than formula (1). Up till now the analysis of the experimental data on the magnetization of glasses has been done only on the basis of the law (1), which is typical of nonband ferromagnets. In these studies the majority of authors have noted the following contradiction: The experimental values<sup>4,5</sup> of the coefficient  $D$  do not agree with the values of the parameter  $A$  found by neutron diffraction studies.<sup>6</sup> As a rule, the values of  $D$  calculated by formula (2) are about 30% smaller than the observed values. This is true at least for iron-rich amorphous alloys ( $\text{Fe}_{80}\text{B}_{20}$ ,  $\text{Fe}_{80}\text{P}_{16}\text{B}_4\text{C}_3$ ,  $\text{Fe}_{75.4}\text{B}_{14.2}\text{Si}_{10.4}$ ); the only exception we know of is the nickel-rich alloy  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ , in which, according to Kaul,<sup>7</sup> the experimental values of the parameters  $D$  and  $A$  are mutually consistent.

In view of what we have said about crystalline  $3d$  metals, it is natural to attempt an interpretation of the experimental data on amorphous  $3d$  alloys using formula (3). By assuming here that the coefficient  $D$  is related to the parameter  $A$  by equation (2), we automatically remove the contradiction between the neutron diffraction experiments and the magnetization measurements. The coefficient  $G$  in (3) is chosen according to the requirement that curve (3) be closest (in the least-squares sense) to the empirical curve  $M(T) = M(1 - BT^{3/2})$ , where  $M \equiv M(0)$ . If a magnetiza-

TABLE I. The magnetic properties of typical glasses.

Material	$T_c$ , K	$M/M_0$	$B/B_0$	$D/D_0$	$A/A_0$	$G/G_0$
$Fe_{80}B_{20}$	685	0.74	6.47	4.53	0.45	2.23
$Fe_{80}P_{16}B_4C_3$	590	0.69	7.35	5.14	0.43	2.53

tion is observed in the experiment in the temperature interval  $(0, T_1)$ , then we have for  $G$

$$G = 2.4(B - D)T_1^{-1/2} \quad (4)$$

Unfortunately, we do not have available a complete set of the necessary experimental data  $(A, B, M)$  for a single amorphous ferromagnet. In the case where both  $B$  and  $A$  are known from experiment (see Refs. 1, 6), it turns out that  $D \sim 0.7B$ ; we therefore reconstruct the value of  $A$  from the known value of  $B$  under the assumption that  $D = 0.7B$ . The empirical values of the parameters for two typical ferromagnetic glasses are given in Table I. As a reference material we have chosen bcc crystalline iron; the parameters of this material are indicated by the subscript zero. The data for iron are:  $T_c = 1042$  K,  $M_0 = 1719$  G,  $B_0 = D_0 = 3.4 \cdot 10^{-6}$  K $^{-3/2}$ ,  $A_0 = 280$  meV $\cdot\text{\AA}^2$ ,  $G_0 = 0.44T_c^{-2}$ .

Let us give the relations we shall need from the theory of band magnetism. For the magnetization  $M$  and coefficient  $G$  we have<sup>2</sup>

$$\mu = \mu_B g \Delta, \quad G = \xi_1 \Delta^{-2}, \quad (5)$$

and the dispersion parameter  $A$  is<sup>8</sup>

$$A = \xi_2 \Delta^{-1} v^2, \quad (6)$$

where  $\Delta$  is the energy of the exchange splitting of the spectrum of the magnetic electrons at  $T = 0$ ,  $g$  is the density of levels at the Fermi surface,  $v$  is the Fermi velocity, and  $\xi_1$  and  $\xi_2$  are numerical factors of order unity, which are specified by the dispersion relation of the magnetic electrons. Relations (5) and (6) enable one to use the data on  $A$ ,  $G$ , and  $M$  to reconstruct the characteristics of the magnetic electrons:

$$\Delta/\Delta_0 = (G_0/G)^{1/2}, \quad g/g_0 = MG^{1/2}/M_0G_0^{1/2}, \quad v^2/v_0^2 = AG^{1/2}/A_0G_0^{1/2}. \quad (7)$$

The numerical values of these quantities are given in Table II. The Curie temperature, we might note, differs from  $\Delta$  only by a coefficient of unit order, i.e.,  $T_c = \xi_3 \Delta$ .

## 2. SPECTRA OF MAGNETIC ELECTRONS IN METALLIC GLASSES

According to Table II, the density of states for magnetic electrons in noncrystalline metals is approximately the same as in crystalline metals, and the quantities  $\Delta$ ,  $M$ , and  $T_c$  are approximately proportional to one another. What seems unexpected at first glance is the significant (approximately two-fold) decrease in the Fermi velocity.

TABLE II. Parameters of the magnetic electrons in typical glasses.

Material	$\Delta/\Delta_0$	$g/g_0$	$v^2/v_0^2$
$Fe_{80}B_{20}$	0.66	1.1	0.30
$Fe_{80}P_{16}B_4C_3$	0.63	1.1	0.27

Turning now to an analysis of these facts, we note that a noncrystalline metal differs from a crystalline one in two closely related aspects. First, because of the significant (in comparison with the crystalline case) fluctuations in the shape and dimensions of the Wigner-Seitz cell, significant fluctuations arise in the interatomic distance. Second, for the same reason, glasses have a higher microscopic symmetry than crystals. Let us first estimate the role of the fluctuations in the interatomic distance. The energy bands that arise in the electron distribution of condensed matter result from the overlap of the electron shells of the individual atoms; therefore, in order of magnitude

$$\Gamma_i = \varepsilon_i \exp \{-l_0/a_i\},$$

where  $\varepsilon_i$  is the energy level of an isolated atom,  $a_i$  is the radius of the corresponding electron shell,  $\Gamma_i$  is the width of the band, and  $l_0$  is the interatomic distance. In a noncrystalline metal the interatomic distance  $l = l_0 + \delta l$  will be a stochastic variable. Since there is a finite (let us assume small) probability of very large values of  $|\delta l|$ , the electronic density of states  $g(\varepsilon)$  does not go to zero even far from the center of the band. Therefore, the electron energy distribution of amorphous solids does not break up into distinct allowed and forbidden bands (see Ref. 9):  $g(\varepsilon)$  is a continuous (though not monotonic) function of  $\varepsilon$ , having sharp peaks which can somewhat conditionally be called energy bands.

The smearing of the  $i$ -th band due to fluctuations is proportional to

$$\varepsilon_i \exp \{a_i^{-1} (\langle \delta l^2 \rangle)^{1/2}\}$$

(the angle brackets denote an average). The minimum  $\langle \delta l^2 \rangle$  is realized in well-annealed samples and is governed by thermodynamic fluctuations that are frozen-in at the melting temperature  $T_m$ . In this case

$$\langle \delta l^2 \rangle = l_0^2 T_m n_0 Y^{-1},$$

where  $n_0$  is the density and  $Y$  is the Young's modulus. Usually  $T_m \sim 1000$  K, and therefore  $(\langle \delta l^2 \rangle)^{1/2} \sim 0.1 - 0.15 l_0$ . Since the radii of the  $3d$  shells is  $a_d \sim 0.5 l_0$ , the smearing of the  $3d$  bands should amount to  $\sim 0.2 - 0.3 \Gamma_d$ . This value, though small in comparison with  $\Gamma_d$ , is not small in comparison with the widths and separations of the individual  $3d$  subbands. Fluctuations of the interatomic distances therefore promote the total or partial fusion of the subbands.

Let us now analyze the change of the microscopic symmetry upon amorphization. The collectivized electrons feel the shape and orientation of the Wigner-Seitz cell not of one, but of a number of atoms of the material. As a result of the averaging over the orientation of these cells, the actual molecular field on the electrons is more symmetric than the crystal field in the corresponding crystal.

It is known that in crystals of cubic symmetry the crystal field lifts the 5-fold degeneracy of the  $d$  band, splitting it into a doubly degenerate subband  $e_g$  and a triply degenerate subband  $t_{2g}$  (we are speaking of the degeneracies in addition to the spin degeneracy). In an amorphous material the splitting of the  $d$  band should be significantly diminished, and can perhaps become smaller than the width of each of the subbands. This tendency is enhanced by the broadening of

the individual subbands due to fluctuations of the interatomic distance, which we mentioned earlier. As a result, the subbands of the  $3d$  band may overlap, and we return to the 5-fold degenerate energy band associated with the case of spherical symmetry (see Ref. 10 in this regard). If  $g_1$  is the density of states at the Fermi surface before fusion of the subbands, the density of states of the  $d$  electrons after the fusion turns out to be  $g = \nu g_1$ , where  $\nu = 5/2$  or  $\nu = 3/2$  depending on which of the subbands the Fermi level fell in prior to their fusion (in view of the semiquantitative nature of the discussion we shall not distinguish these cases, but take  $\nu = 2$ ). We now make use of the empirical fact that  $g/g_0 \sim 1$ ; this fact stems from the rough proportionality that is observed among the values of  $M$ ,  $G$ , and  $T_c$ . Let us suppose for simplicity that the effective mass  $m = (\partial\varepsilon/\partial p)^{-1}p$  does not depend on  $\varepsilon$ ; then  $g$  is proportional to  $v$ . Thus, from the relation  $2g_1 \approx g_0$  we immediately find that  $v^2/v_0^2 \sim 0.25$ , which is close to the empirical value (see Table II). The decrease in the Fermi velocity of the  $3d$  electrons may thus be a consequence of the fusion of the  $3d$  subbands in the electron energy distribution of metallic glasses.

It should be noted that the decrease in the Fermi velocity of the  $3d$  electrons upon amorphization leads, according to (6), to a decrease in the coefficient  $A$  in the spin-wave dispersion relation—to a softening of the spin wave. This softening of the spin wave is well known in experiment (see Ref. 1) but, in our view, has never before been convincingly explained.

## CONCLUSIONS

1. By interpreting the experimental temperature dependence of the magnetization of ferromagnetic glasses in ac-

cordance with the theory of band magnetism [formula (3)], one can eliminate the contradiction between the experimental values of the magnon dispersion parameter  $A = \omega/k^2$  and the coefficient  $D$  in the Bloch three-halves law.

2. The experimentally observed softening of the spin wave (the significant decrease in the parameter  $A$  in comparison with the crystalline case) is now seen to be a consequence of the fusion of the subbands of the  $3d$  band in the electron spectrum of glasses.

3. The model could be checked by direct observation of the shape of the  $3d$  band in metallic glasses.

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