by interference effects, a number of parameters were adjusted in an attempt to achieve a fit. The theory failed to describe certain observed spectral features, and it is ambiguous whether the deviations were associated with damping. An experiment on soft polaritons in LiNbO₃ has recently been published by Rokni *et al.* (Ref. 8), but the paper differs greatly in spirit from ours, and a detailed line-shape analysis is not presented.

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Model for the Origin of Ferromagnetism in Fe: Average-Moment Internal-Field Variations in *Fe*Si and *Fe*Al Alloys

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A detailed indirect-coupling model is given for the origin of ferromagnetism in Fe. With no free parameters this model describes the difference in behavior of the average moments and hyperfine fields in *Fe*Si and *Fe*Al alloys. The hyperfine-field results lead to a possible operational distinction between localized and nonlocalized *d* electrons.

I. INTRODUCTION

Ever since the early sixties it has been realized that ferromagnetism in Fe arises from indirect exchange coupling of the magnetic ions, when calculations of the direct interaction showed that this mechanism was too small[1] and of the wrong sign.[2] Furthermore there is strong experimental evidence that the major portion of the Fe moment is localized. This evidence comes from neutron scattering[3] experiments, specific-heat measurements[4] which gave an entropy associated with the transition through the Curie temperature of $Nk \ln 3$, and equality of the high-temperature moment and the saturation moment[5] of Fe. This indicates that the intra-atomic coupling in Fe is considerably larger than the coupling between moments.[6]

Some indirect coupling between the magnetic ions takes place through the 4s-like itinerant electrons. The polarization of the 4s electrons has been measured directly by Mössbauer[7] and by NMR[8] experiments, by measuring the hyperfine-field behavior with alloying. While the net polarization was found to be $+0.05$ to 0.08%,[8] the polarization at the first ($N1$) and second ($N2$) neighbors is dominant and negative (opposite to the Fe moment) and thus would tend to make Fe antiferromagnetic. Therefore we infer that the ferromagnetism arises from a long-range Ruderman-Kittel-Kasuya-Yosida (RKKY)-type[9]

indirect exchange interaction of the itinerant 3d-like electrons. We can reasonably estimate an *upper limit* for the number of these itinerant *d* electrons. Since the first- and second-neighbor shells are very close together in a bcc lattice and since Fe is a rather stable ferromagnetic (for instance upon alloying) the first node of the itinerant *d*'s RKKY-like oscillation cannot be in closer than about the third-neighbor ($N3$) shell. Assuming then that it is at the $N3$ shell we find from the form of the RKKY function (treating the itinerant *d*'s as free electrons) that an upper limit to the total number of itinerant *d*'s is about 0.34 per atom. Assuming that this itinerancy character is equally divided among the seven *d* electrons in Fe yields an upper limit of the fraction of itinerancy for each *d* electron of 0.05. Thus an *upper limit* to the amount of itinerant moment in Fe is 0.1 μ_B. This agrees with the above-mentioned observations that the Fe moment is essentially localized.

Owing to the complex nature of the theory of ferromagnetism it has been impossible to theoretically derive the amount of locality or nonlocality of the 3d wave functions.[10] In fact even the definition of what is meant by local or itinerant electrons is obscure in the theories. We shall show that hyperfine-field measurements on the other hand lead to a simple operational distinction between localized and itinerant electrons. Since the itinerant *d* electrons have strong

overlap with the localized d's while the $4s$-like conduction electrons have little if any overlap with the d wave functions the moment of an Fe atom is essentially locked in by the itinerant d's. Thus while the $4s$-like electrons do not have any appreciable effect on the magnetization or total spin of Fe, for such an atom with quenched orbital momentum, they do completely dominate the hyperfine field. Using this model (mainly localized d's ferromagnetically coupled by the itinerant d's and antiferromagnetically coupled by the $4s$-like electrons) we derive, with no unknown parameters, the observed behavior of the average hyperfine fields in FeSi and FeAl (0–15 at.%) alloys.

II. AVERAGE MOMENT

We will consider only Si and Al solute atoms since we know they develop no moment and fit nicely into the Fe lattice without any overlap polarization.[8] [As discussed in Ref. 8(b), Al may have a very slight amount of overlap or volume misfit polarization so that only Si is really the ideal case.] Iron is known to have about one $4s$ conduction electron per atom.[6,8] As we alloy with Si or Al one of their outer s electrons is presumed to go into the conduction band while the other outer electrons stay near the solute atom shielding the excess charge.

As discussed in the Introduction we assume that the moment is aligned by only the spin-density RKKY-like function describing the itinerant d's. Thus surrounding an Fe atom we have a spin polarization of the itinerant d's of the well-known RKKY form[9] given by

$$\vec{\Delta\rho_d}(R) = \left(\frac{9\pi n}{E_F}\right) J_d(0) \vec{S} F(R) , \qquad (1)$$

where $\Delta\rho_d(R)$ and $J_d(0)$ are the fractional polarization and exchange integral of the itinerant d's, n is the number, E_F is the Fermi energy of the itinerant d's, and S is the spin of the magnetic ion ($S \simeq 1$ in a pure Fe lattice). $F(R)$ is the usual oscillatory function and since we will only evaluate it at lattice points:

$$F_n^d(R_n) = \frac{2k_F^d R_n \cos(2k_F^d R_n) - \sin(2k_F^d R_n)}{(2k_F^d R_n)^4} . \qquad (2)$$

Actually, in what follows we do not care what the detailed behavior of $F_n^d(R_n)$ is, just that it falls off rather rapidly. We have a similar function $\Delta\rho_s$ to describe the spin polarization of the $4s$ conduction electrons surrounding an Fe atom. However its form has been measured and we will use these values as given in Ref. 8.

First let us evaluate the average moment $\overline{S}_i(x)$ in an alloy with a concentration x of Si or Al atoms. We can show that no matter what the fraction f of itinerant electrons the moment behavior in the alloy follows simple dilution. If all the d electrons were

itinerant (the amount of polarization due to s electrons is very small and will be neglected[8]) then in pure Fe each shell would produce a contribution to the polarization or moment proportional to $N_j F_j^d$, where N_j is the number of sites in the jth shell. So the total moment would be proportional to $\sum_j N_j F_j^d$. Taking $S_{Fe} \simeq 1$ we thus obtain the average moment for an alloy by summing over the contribution from each shell. This is given by

$$\overline{S}_i(x) = \sum_{m_1=0}^{N_1} \cdots \sum_{m_n=0}^{N_n} \left[\sum_{j=1}^{n} m_j F_j^d \prod_{k=1}^{n} p(m_k, N_k, x) \right]$$

$$\times \left(\sum_{j=1}^{n} N_j F_j^d \right)^{-1} , \qquad (3)$$

where m_j is the number of Fe atoms in the jth shell and $p(m_k, N_k, x)$ is just the probability of finding m_k Fe atoms in the kth shell which contains N_k sites. It is the usual binomial probability given by

$$p(m, N, x) = \binom{N}{m} (1-x)^m (x)^{N-m} . \qquad (4)$$

Using the relations

$$\sum_{m=0}^{N} p(m, N, x) = 1 ,$$

$$\sum_{m=0}^{N} m p(m, N, x) = N(1-x) \qquad (5)$$

repeatedly, Eq. (3) simply becomes

$$\overline{S}_i(x) = (1-x) . \qquad (6)$$

On the other hand if nearly all the d electrons were localized they would be aligned by the small fraction of itinerant d's but there would only be a fraction $1-x$ of them so that again the average moment would be $(1-x)S_{Fe}$. If there were any fraction f of itinerant electrons the localized fraction would give rise to a moment $(1-f)(1-x)S_{Fe}$ and from Eq. (6) the itinerant fraction would give rise to a moment of $f(1-x)S_{Fe}$ so that again the total moment would be $(1-x)S_{Fe}$. Thus as is well known an average moment measurement is incapable of giving any information as to the distinction between localized and nonlocalized d electrons. We will see below that the hyperfine-field measurements are of a different nature, such that they can actually distinguish between localized and itinerant d electrons. The measured average moments[11] for FeSi and FeAl alloys are shown along with the dashed line $(1-x)$ in Figs. 1 and 2. We see that these alloys follow simple dilution very well.

III. AVERAGE HYPERFINE FIELD

Since Si and Al solute atoms develop no moment and have essentially no volume overlap, the hyperfine field at an Fe atom in these alloys, being due to s electrons only, contains only two terms:
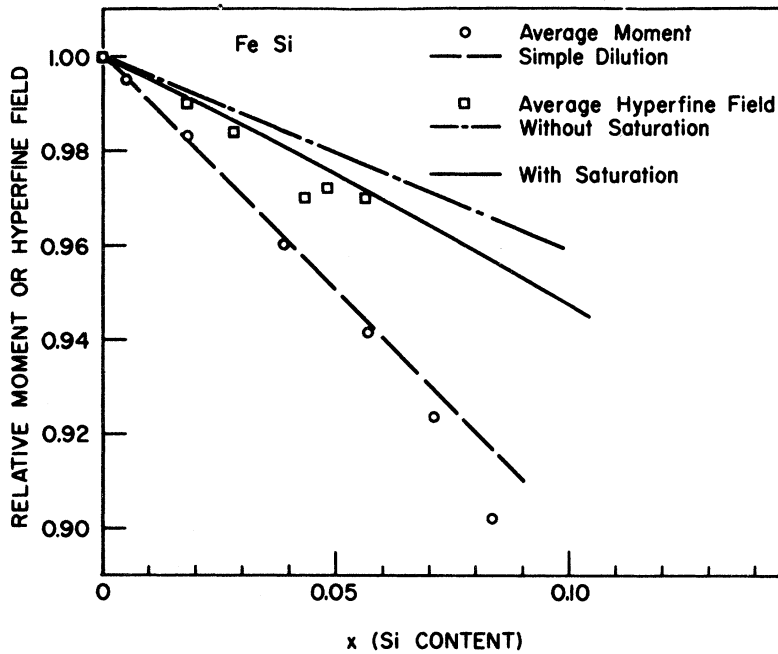
FIG. 1. Variation of average moment and average hyperfine field of FeSi alloys as a function of at.% Si. The dashed curve is the moment expected for simple dilution. The solid curve is the variation of the average hyperfine field expected from indirect-exchange interactions.

$$H = H_{cp} + H_{ce} \quad . \tag{7}$$

The first term is due to the core polarization of the inner s electrons by the d electrons, and the second is due to the polarization of the $4s$ conduction electrons. This latter term can be further split into two terms; a self-polarization field H_s due to the polarization by the atom itself and a field due to the polarization by all the surrounding neighbors H_C. In pure Fe

$$H_C^{Fe} = \sum_{j=1}^{n} N_j \, \Delta H_j^{Fe} \quad , \tag{8}$$

where we sum over n neighboring shells and N_j is the number of sites in the jth shell. The ΔH_j^{Fe} have been measured in Refs. 7 and 8 and are listed in Table I. Thus the field at an atom in pure Fe is given by

$$H_{Fe} = H_{cp}^{Fe} + H_s^{Fe} + \sum_{j=1}^{n} N_j \, \Delta H_j^{Fe} \quad . \tag{9}$$
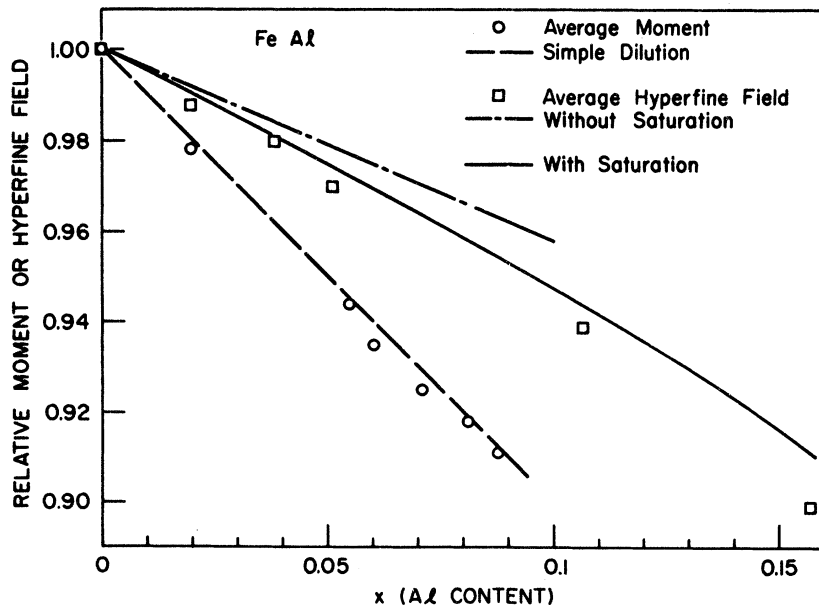

FIG. 2. Variation of average moment and average hyperfine field of FeAl alloys as a function of at.% Al. The dashed curve is the moment expected for simple dilution. The solid curve is the variation of the average hyperfine field expected from indirect-exchange interactions.

TABLE I. Hyperfine-field contributions from the various neighbor shell in pure Fe.

Shell j	N_j	$\Delta H_j^{Fe}/H_{Fe}$
1	8	$+0.08$
2	6	$+0.018$
3	12	-0.016
4	24	-0.004
5	8	-0.002
6	6	-0.004

In an alloy with a fraction x of Si or Al atoms the hyperfine field at the ith Fe atom is

$$H_i(x) = H_{cp}^i(x) + H_s^i(x) + H_{Cj}(x) \ .$$

It is at this point that we clearly have to decide whether the moment is localized or itinerant. If it is essentially all localized then all the Fe atoms have $H_{cp}^i = H_{cp}^{Fe}$ and $H_s^i = H_s^{Fe}$ no matter what the concentration x is. That is these terms do not average over the alloy but depend only on the lattice cell containing the Fe atom. If it were all nonlocalized then we would have

$$H_{cp}^i(x) = \overline{S}(x)H_{cp}^{Fe} = (1-x)H_{cp}^{Fe}, \quad H_s^i(x) = (1-x)H_s^{Fe} \ .$$

As we shall see the two different assumptions lead to very different results for the average hyperfine field. So the simple operational definition of locality or nonlocality just becomes the following: If the core and self-polarization effects come from only the lattice cell containing the atom the moment is called localized; if they come from neighboring shells as well the moment is to that extent nonlocalized.

As discussed above the correct assumption which leads to Fe being ferromagnetic is that nearly all of the moment has localized character with an *upper limit* of nonlocal d-like character of $0.1 \mu_B$. Thus

$$H_i(x) = H_{cp}^{Fe} + H_s^{Fe} + H_{Cj}(x) \ . \tag{10}$$

We can eliminate H_{cp}^{Fe} and H_s^{Fe} (although they were evaluated in Ref. 8) by using the pure Fe hyperfine field in Eq. (9). We thus get

$$H_i(x) = H_{Fe} - \sum_{j=1}^{n} N_j \Delta H_j^{Fe} + H_{Cj}(x) \ . \tag{11}$$

Since we want the average hyperfine field we take the average of Eq. (11) by finding the average of $H_{Cj}(x)$. This is obtained by summing the $\Delta H_j(x)$ (since all moments have the same value as in pure Fe) over all possible occupational configurations. Let us first assume that $\Delta H_j(x) = \Delta H_j^{Fe}$. Then we obtain

$$\overline{H}_{Cj}(x) = \sum_{m_1=0}^{N_1} \cdots \sum_{m_n=0}^{N_n} \left[\sum_{j=1}^{n} m_j \Delta H_j^{Fe} \prod_{k=1}^{n} p(m_k, N_k, x) \right] \ . \tag{12}$$

Again using Eqs. (5) repeatedly this simply reduces to

$$\overline{H}_{Cj}(x) = (1-x) \sum_{j=1}^{n} N_j \Delta H_j^{Fe} \ . \tag{13}$$

Thus we finally obtain, for the average hyperfine field,

$$\frac{\overline{H}_i(x)}{H_{Fe}} = 1 - x \sum_{j=1}^{n} \frac{N_j \Delta H_j^{Fe}}{H_{Fe}} \ . \tag{14}$$

The values of $\Delta H_j^{Fe}/H_{Fe}$ have been measured[7,8] and are given in Table I. The signs are opposite to those in Ref. 7 because there they were given relative to the direction of the Fe moment; since H_{Fe} is negative $\Delta H_1/H_{Fe}$ is positive. Using these values and going out to $n = 6$ (we assume the shifts are small and tend to cancel each other beyond the 6th shell), we find

$$\sum_{j=1}^{6} \frac{N_j \Delta H_j^{Fe}}{H_{Fe}} = + 0.42 \ . \tag{15}$$

We thus obtain

$$\overline{H}_i(x)/H_{Fe} = 1 - 0.42x \ . \tag{16}$$

Thus the average field should not fall as fast as the average moment; it only decreases by the fraction of the total internal field that is due to the sum of the conduction-electron contribution due to the neighbors. Thus substituting in an Si or Al atom for Fe decreases the moment by one full Fe moment while it only decreases the hyperfine field by 0.42 of the total hyperfine field. Equation (16) is shown as the dot-dashed curve in Figs. 1 and 2. We see that this curve is somewhat above the measured average hyperfine field. This is to be expected since in deriving Eq. (12) we assumed that there were no saturation effects, i.e., that two Fe atoms missing from a given shell had twice the effect of one missing Fe atom. We know that this is not so and that indeed we have rather strong magnetic-shielding effects. If a shell is full all the Fe atoms tend to shield the effects of the others and the change in hyperfine field upon removing the first Fe atom is smaller than that of removing the second, etc. This shielding or saturation effect has been measured in Ref. 8, and some measured saturation data are shown in Fig. 7 of Ref. 8. The effect is complex in that we have both intershell and intrashell shielding. However the intrashell behavior for all shells seems quite similar and can be represented quite well by

$$\Delta H_j(m) = (4/m^q)\Delta H_j^{Fe} \ , \tag{17}$$

where $q = \ln 4/\ln N_j$ and m is the number of Fe atoms in the jth shell. This function is shown plotted in Fig. 3 for $N_j = 8$, 6, and 12 as would occur in the first three neighbor shells. It reproduces the measured behavior of the $N2$ shell (see Fig. 7 of Ref. 8) very well. We see that for one Fe atom
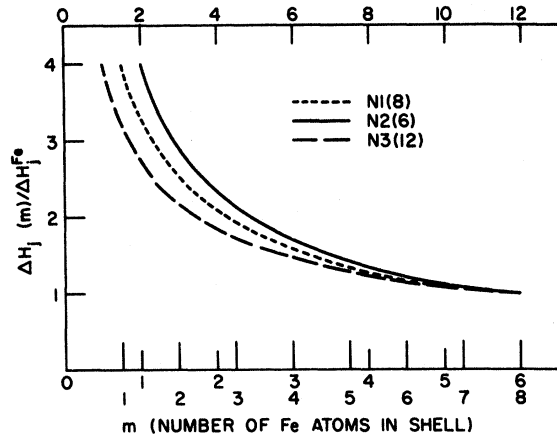
FIG. 3. Hyperfine-field shift due to removing one Fe atom from a shell containing m Fe atoms, as measured in Ref. 8.

left in a shell $(m = 1)$ the field shift is four times that for a full shell and decreases smoothly to ΔH_j^{Fe} for a full shell. We now estimate the saturation effects as follows. We know from Eq. (14) that the hyperfine field decreases by the sum of the shifts due to the missing Fe atoms. We now take this sum including the saturation effects. Thus the hyperfine-field decrease becomes

$$\Delta H_T(x) = \sum_j \sum_k (N_j - m_k) p(m_k, N_j, x) \Delta H_j(m_k) \ .$$
(18)

Letting $\Delta j(m_k)$ be the added hyperfine-field shift over that in pure Fe due to removing one Fe atom from the jth shell containing m_k Fe atoms, it is given by

$$\Delta j(m_k) = [4/(m_k)^q - 1] \Delta H_j^{Fe} \ .$$
(19)

Using the relation

$$\sum_{m=0}^{N} (N - m) p(m, N, x) = Nx \ ,$$

we get a hyperfine field decrease of

$$\Delta H_T(x) = x \sum_j N_j \Delta H_j^{Fe}$$

$$+ \sum_j \sum_k (N_j - m_k) p(m_k, N_j, x) \Delta j(m_k) \ . \quad (20)$$

We can readily evaluate the second term on a computer, and we obtain the values listed in the second column of Table II. The third column gives the total hyperfine-field decrease, Eq. (20), and these values are shown by the solid curves in Figs. 1 and 2. We see that the intrashell saturation correction brings the calculated curve quite close to the measured average hyperfine-field values. However we have not taken into account intershell saturations which were also observed to exist, see Ref. 8. This would further lower the calculated curve a slight

amount. Thus the agreement between this "localized-moment" indirect-coupling model and the measured average hyperfine fields is very good.

Let us see what result would have been obtained if we had assumed all the moment was nonlocalized. Then the hyperfine field at the ith Fe atom would be

$$H_i(x) = (1 - x)(H_{cp}^{Fe} + H_s^{Fe}) + H_{Dj}(x) \ ,$$

where now $\overline{H}_{Dj}(x)$ will be given by (neglecting saturation effects)

$$\overline{H}_{Dj}(x) = \overline{S}(x) \sum_{m_1=0}^{N_1} \cdots \sum_{m_n=0}^{N_n} [m_j \Delta H_j^{Fe} \prod_{k=1}^{n} p(m_k, N_k, x)] \ .$$

Using Eqs. (5) repeatedly this becomes

$$\overline{H}_{Dj}(x) = (1 - x)^2 \sum_{j=1}^{n} N_j \Delta H_j^{Fe} \ .$$
(21)

The average field $\overline{H}_i(x)$ is thus

$$\frac{\overline{H}_i(x)}{H_{Fe}} = (1 - x) \left(1 - x \sum \frac{N_j \Delta H_j^{Fe}}{H_{Fe}} \right) \ .$$
(22)

Thus the average hyperfine field is depressed from the simple dilution behavior by the sum of the fields from the missing Fe atoms. As is clearly seen from Figs. 1 and 2 this is not the case and indeed the d electrons causing the moment must be overwhelmingly localized (in the sense described above). We can also easily derive the formula for the average hyperfine field for any fraction f of itinerant electrons. It is (without saturation effects)

$$\frac{\overline{H}_i(x)}{H_{Fe}} = (1 - fx) \left(1 - x \sum_j \frac{N_j \Delta H_j}{H_{Fe}} \right) \ .$$
(23)

Thus if $\overline{H}_i(x)$ and the ΔH_j are measured we can obtain an estimate of f. Taking into account the intrashell saturation only we could interpret the difference between the calculated solid curves of Figs. 1 and 2 as due to itinerant d electrons and obtain an independent estimate of f. (Actually this is again an upper limit since as mentioned above some of the deviation could be due to intershell saturation effects.) Doing this, using the values listed in

TABLE II. Variation of intrashell saturation effects, ΔH_{sat} [the second term of Eq. (20)] and the total hyperfine field ΔH_T decrease with solute concentration x.

x	ΔH_{sat}	ΔH_T
0.02	0.001	0.010
0.04	0.003	0.020
0.06	0.005	0.030
0.08	0.008	0.042
0.10	0.011	0.053
0.15	0.021	0.084

Table II, we get an upper limit for the fraction of itinerancy in the d electrons of 0.04.

Let us discuss briefly the expected behavior of other solute atoms. Solute atoms that either develop a moment or have volume overlap effects will distort the spin-density polarization functions of the s and d electrons, and we would thus not expect their moments to follow simple dilution or their average hyperfine fields to follow Eq. (11). The degree of distortion is difficult to predict but we can turn the problem around and get a sense of the distortion from the degree the average moment does not follow simple dilution. As expected from the above criteria and discussed in Ref. 8 most elements would not be expected to and do not show simple dilution. An interesting controversial case[12] is Mn which does follow simple dilution fairly well (to 4%) and starts out decreasing as Eq. (20) (to ~ 4%) but then deviates. This does not necessarily indicate

that the Mn atom develops very little moment in dilute FeMn alloys.

IV. CONCLUSIONS

The decrease of the average hyperfine field in dilute Si and Al alloys of Fe can be attributed to the loss of the $4s$-like conduction-electron hyperfine-field contribution of the missing Fe neighbors. Since the Fe hyperfine field is only partially due to the $4s$ conduction-electron contribution of the neighbors, the average hyperfine field falls less rapidly than the moment in these alloys. A model for Fe is proposed where the Fe moment is essentially localized, and these moments are ferromagnetically aligned by a slight amount (< 0.04 per d electron) of d-like itinerant electrons. The $4s$-like conduction electrons tend to align Fe antiferromagnetically. The hyperfine-field measurements appear to be able to distinguish between local and nonlocal moments.

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