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SOME REGULARITIES OF THE MAGNETIC FIELDS AT NUCLEI OF IMPURITY ATOMS IN FERROMAGNETIC SUBSTANCES

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The interrelation between the magnetic field strengths at impurity-atom nuclei in metallic ferromagnetic matrices with an electron impurity structure is considered. It is shown that the main parameters determining the magnitude and sign of the field are the number of external s, p, and d electrons and the number of electrons in the filled shells of the impurity atom. An analysis of the observed regularities indicates that electrons of the filled shells make the biggest contribution to the magnetic field strength. The polarization of the impurity atom depends on the number of external electrons. However, the direct contribution of these electrons (as well as those of the conduction band of the matrix) to the magnetic field on the nucleus is small. A simple empirical formula is derived and describes satisfactorily the experimental data. The results lead to some conclusions regarding the strength and the sign of the magnetic field in those cases when no experimental data are available.

INTRODUCTION

THE intensities of the magnetic fields acting on nuclei of impurity atoms in metallic ferromagnetic matrices (Fe, Co, Ni) have been measured for 35 elements (disregarding the rare-earth elements, which are not considered in this article). At the same time, it is impossible at present to carry out a consistent theoretical analysis of the experimental data. Moreover, it cannot even be assumed that the cause of the magnetic fields at the nuclei is understood even qualitatively. Therefore, particular significance attaches to a search for empirical regularities capable of contributing to a well-founded choice of the possible mechanisms producing the fields, and serving as a stimulus for theoretical investigations in this region.

The first attempt of this type was made by Shirley and Westenbarger[1], who considered the interaction between the values of the magnetic field and the constants of the atomic hyperfine structure. They reached the conclusion that the main mechanism producing the magnetic field at the impurity-atom nucleus is connected with polarization of the conduction electrons that produce the magnetic field as a result of contact interaction. Frankel et al.[2] called attention to the systematic change of the field as a function of the number of external p-electrons for elements with Z = 49–52. Kogan[3] considered the correlation between the magnetic field intensities and the radius of the impurity atom.

In this article we shall show that a more general approach to the analysis of the experimental data is possible. The values of the magnetic fields at the nuclei of impurity atoms obey definite laws, which will be considered in the next section of the article. The simplicity of these laws makes it possible to represent the results of the measurements in the form of an empirical formula that describes well the experimental data. The interpretation of the observed laws allows us to draw certain new conclusions concerning the nature of the occurrence of magnetic fields at nuclei. In particular, it can be stated that the main contribution of the magnetic field is made not by the external electrons (or the electrons of the conduction band), but by the electrons of the filled shells of the impurity atom.

Experimental data on the magnetic fields at the impurity-atom nuclei employed in the present analysis are listed in the table. Where several measurements whose results agreed with one another were available, we averaged the results. If the results of the measurements by different workers were contradictory, they were disregarded. The laws discussed below do not include data for Fe, Mo, and Re (in all three matrices), and also for Mn and Co in an Ni matrix. For the corresponding values of the magnetic fields are in a certain sense "anomalous" and do not agree very well with the general laws. These cases amount to only 13% of the total, so that their exclusion does not affect greatly the generality of the results. The possible causes of such "anomalies" will be considered below.

FUNDAMENTAL EMPIRICAL LAWS

1. Proportionality of the Magnetic Field at the Nucleus of the Impurity Atom to the Magnetic Moment of the Matrix Atoms

In most cases the magnetic field at the nucleus of the impurity atom is proportional, with a good degree of accuracy, to the atomic magnetic moment of the matrix. This law is well known, and will therefore not be discussed here in detail. It was first noted for Au impurity atoms by Roberts and Thomson[4], and later (for the majority of cases) by Shirley and Westenbarger[1]. The ratio of the field H to the magnetic moment μ of the matrix atoms (μ = 2.2, 1.7, and 0.6 for Fe, Co, and Ni respectively) is usually constant within not worse than 10–20%. An appreciable deviation from the proportionality of H and μ takes place for V and Sn; in these cases, however, the fields are very weak, and therefore

Magnetic field (kOe) at impurity-atom nuclei for the elements of groups IV, V, and VI

Period IV	ν	Matrix Fe	Co	Ni	Period V	ν	Matrix Fe	Co	Ni	Period VI	ν	Matrix Fe	Co	Ni
Sc	3	(+)100	—	—	Y	3	+286	—	—	La	3	—	—	—
Ti	4	—	—	—	Zr	4	—	+90	—	Hf	4	—	—	—
V	5	—87	—48	(—)7,5	Nb	5	—242	—189	—40	Ta	5	—250	—	—94
Cr	6	—	—	—	Mo	6	—256	(—)150	(—) 40	W	6	—710	—366	—75
Mn	7	—225	—135	—320	Tc	7	—	—	—	Re	7	—600	—440	—95
Fe	8	—339	—317	—282	Ru	8	—505	—415	—178	Os	8	(—)1140	(—)870	(—)300
Co	9	—290	—215	—120	Rh	9	—544	—400	—	Ir	9	—1240	(—)965	(—)440
Ni	10	—235	—189	—75	Pd	10	—597	—402	—184	Pt	10	—1200	—820	—350
Cu	11	—215	—157	—46	Ag	11	—336	—	—95	Au	11	—1315	—960	—330
Zn	12	—	—	—	Cd	12	—348	—	—65	Hg	12	—980	—	—
Ga	13	(—)110	(—)62	—	In	13	—291	—	—37	Tl	13	—	—	—
Ge	14	—	—	—	Sn	14	—81	—21	+19	Pb	14	+262	—	—
As	15	—	—	—	Sb	15	+240	+187	+90	Bi	15	—	—	—
Se	16	—	—	—	Te	16	+620	+550	+195	Po	16	—	—	—
Br	17	—	—	—	J	17	(+)1130	—	—	At	17	—	—	—

Note. The parameter ν is equal to the number of the electrons in the outer shells of the impurity atom. The parentheses indicate that the sign was not measured, but can be established on the basis of the general laws.

the absolute deviations from proportionality are comparable with the deviations for other elements.

The proportionality of H and μ seems to be natural, but it must be noted that this law is far from trivial. The constancy of the ratio H/μ offers evidence that the magnetic field is insensitive to details of the electron structure of the matrix and of the interaction between the impurity atom and the matrix atoms. For a given impurity, in first approximation, only the value of μ is important. Thus, in the analysis of the magnetic fields, an impurity in a ferromagnetic metal can be regarded as relatively isolated from the matrix. The exchange interaction polarizing the impurity electrons is proportional to μ, but depends on the details of the electron wave functions of the matrices only to a small degree. The exchange-interaction mechanisms that do not satisfy this condition (for example, direct overlap of the wave functions of the external impurity electrons with the wave functions of the d-electrons of the matrix atoms) should not play the decisive role in the analysis of the magnetic fields at the impurity-atom nuclei. The proportionality of the quantities H and μ makes it possible to consider henceforth the fields for all three matrices simultaneously, using the "reduced" magnetic field H/μ.

2. Dependence of the Magnetic Field on the Number of Electrons in the Outer Shells of the Impurity Atom

An interesting and important regularity is observed in the analysis of the dependence of the magnetic field for elements of one period on the number of electrons in the outer shells of the atom (i.e., on the total number of (n – 1)d electrons, ns electrons, and np electrons, where n = 4, 5, and 6 respectively for elements of periods IV, V, and VI). Figure 1 shows such a dependence for elements of period V, the data for which are the most complete. The magnetic fields have maximum negative values for elements in the middle of the period; the fields decrease on approaching the ends of the period, reverse sign, after which an increase of the fields in the negative direction is observed.

We have approximated the observed regularity by means of a parabola that is symmetrical about the middle of the period, of the form

$$H/\mu = a + b(\nu - 9)^2, \qquad (1)$$

where ν is the number of external electrons, and a and b are constant coefficients. As seen from Fig. 1, the experimental points fit this curve very well. For the elements of periods IV and VI, the plots of H/μ against ν have a similar form, differing from the plots shown in Fig. 1 only in the ordinate scale.

It is important that the variation of the field within the limits of one period is determined by the total number of the outer electrons, regardless of whether these are s, p, or d electrons. The symmetry with respect to ν = 9 denotes that this number of outer electrons produces the same field as the corresponding number of holes. The symmetry indicates also that within the limits of one period (in spite of the conclusions of[1]) there is no correlation between the magnitude of the field and the constants of the atomic hyperfine structure. If the field were connected with the constant of the atomic hyperfine structure, then the magnetic fields for elements at the end of the period would be several times larger than for the elements at the start of the period. However, no such direct connection between H and the atomic number Z is observed. We must therefore conclude that the mechanism for the occurrence of the field at the nucleus discussed in[1] (contact interaction with the conduction electrons) has no experimental foundation.

3. Dependence of the Magnetic Field on the Number of the Periodic Group

At a fixed number ν of outer electrons, the value of the magnetic field increases with increasing number of the period. In order to establish the character of this

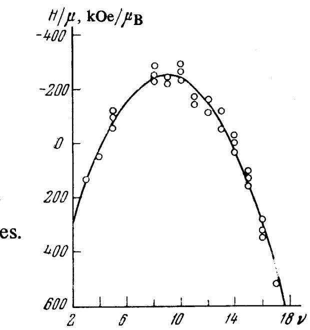

FIG. 1. Dependence of the "reduced" magnetic field on the number of outer electrons for elements of period VI. The solid curve is the parabola a + b (ν – 9)², the coefficients of which were determined by least squares.

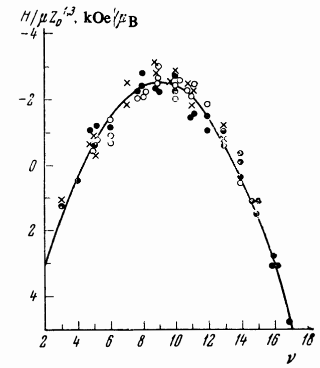

FIG. 2. Comparison of the experimental data for the elements of periods IV (X), V (●), and VI (○) with the dependence calculated in accordance with formula (2) (solid curve).

dependence, we determined by the least squares the coefficients a and b of formula (1) for the elements of all three periods. They turn out to be −108.7 and +4.87 for period IV, −256.6 and +11.3 for period V, and −597.5 and +28.4 for period VI. It is easy to note that when the number of the period is increased by unity, the coefficients a and b increase by approximately the same factor $a_{n+1}/a_n \approx b_{n+1}/b_n = 2.4$. This result is difficult to explain by assuming that the magnetic field is produced by contact interaction with the outer impurity electrons (or with the electrons of the conduction band). At the same time, such a dependence of the field on the number of the period becomes natural if we assume that the main contribution to the magnetic field at the nucleus is made by the electrons of the filled shells. It can be shown[5] that in the approximation of the Thomas-Fermi model the magnetic field at the nucleus, due to the electrons of the filled shell containing Z_0 electrons, is proportional to $Z_0^{1.3}$. The value of Z_0 for the elements of periods IV, V, and VI is respectively 18, 36, and 68. (Z_0 includes the 4f-electrons in the case of the considered elements of period VI.) Consequently, the fields for the elements of period V should exceed those for the elements of period IV by a factor $2^{1.3} = 2.46$. Similarly, for the ratio of the fields for the elements of periods VI and V we obtain $1.9^{1.3} = 2.35$. Both these figures practically coincide with the empirical coefficient 2.4. Thus, the value of the magnetic field is proportional with good accuracy to $Z_0^{1.3}$, where Z_0 is the number of the electrons in the filled shells of the impurity atom.

The foregoing empirical regularities allow us to represent the experimental data for all three matrices and all three periods in the form of a simple formula. To this end, it is sufficient to introduce into relation (1) the coefficient $Z_0^{1.3}$, as a result of which we obtain:

$$H/\mu Z_0^{1.3} = -2.48 + 0.113(\nu - 9)^2. \qquad (2)$$

Figure 2 shows a comparison of the experimental data with formula (2). We see that the values of the fields calculated in accordance with this formula agree well with experiment: for the overwhelming majority of the points, the deviation from the calculated curve does not exceed 20%.

MECHANISM OF OCCURRENCE OF MAGNETIC FIELDS AT NUCLEI OF IMPURITY ATOMS IN METALLIC FERROMAGNETIC MATRICES

The regularities considered above can be explained qualitatively by assuming that the main contribution to the magnetic field at the nucleus is made by the polarized electrons of the filled shells of the impurity atom. As will be seen below the polarization can be produced by two mechanisms of comparable magnitude but opposite sign.

The experimental data show that the negative contribution to the field increases with increasing number of outer electrons or holes, reaching a maximum at $\nu = 9$. The wave functions of the outer electrons are mixed under the influence of the strong exchange field, so that an important parameter is the total number of the outer electrons (without classification by orbital quantum number). The most probable mechanism of polarization of the outer electrons of the impurity atom is their interaction with the polarized electrons of the conduction band of the matrix; the effective magnetic moment acquired by the shell as a result of the polarization is maximal when the shell is half-filled. However, the direct contribution made by the outer electrons to the field at the nucleus is relatively small. This is evidenced by the absence of a direct relation between the field and the atomic number within each period (the absence of correlation with the constant of the atomic hyperfine structure). It is therefore necessary to assume that the negative contribution is a result of polarization of the filled internal shells of the impurity atom by the electrons of the outer shell. The filled internal shells have a larger density in the region of the nucleus than the outer electrons, and it is therefore natural that it is precisely the electrons of the internal shells which make the main contribution to the field on the nucleus. This conclusion agrees with the previously considered dependence of the field on the parameter Z_0.

Besides the negative contribution, there should exist also a positive contribution, which predominates when $|\nu - 9| \gtrsim 5$. Unlike the former contribution, the positive contribution does not depend (or depends weakly) on ν, remaining at the same time proportional to $Z_0^{1.3}$. This shows that the magnitude of the positive contribution is also determined by the polarization of the internal shells, but does not depend on the value of the effective magnetic moment of the outer electrons of the impurity atom. It is natural to assume that such a polarization is caused by direct interaction of the electrons in the filled shells with the polarized electrons of the conduction band of the matrix. The electron polarization of the matrix conduction band should therefore have a sign opposite that of the outer electrons of the impurity atom. Of course, the sign of the polarization of the conduction electrons should be the same for all three matrices. The hypothesis advanced earlier[6] that this polarization can have opposite signs (based only on the data for tin impurity atoms) has not been confirmed.

On the basis of formula (2) we can estimate approximately the magnitudes of each of the two considered contributions to the magnetic field. Formally, extrapolating (2) to $\nu = 0$, we should obtain the magnitude of the field due to the polarization of the internal shells by the electrons of the matrix conduction band. For example, for the elements of period V the corresponding contribution to the "reduced" magnetic field H/μ turns out to be +700 kOe. Then the maximum negative contribution for these elements (at $\nu = 9$) is −960 kOe.

The considered model of the mechanism producing the field reflects the basic and most general laws. In particular, this model presupposes the relative independence of the electron structure of the impurity atom on the electron structure of the matrix. The agreement between the values calculated by formula (2) with the experimental data shows that for most elements this is a good approximation. However, in individual cases there are appreciable deviations from the general laws. For example, an anomalously large negative magnetic field is observed for Mn and Ni[7]. This anomaly is accompanied by the occurrence of a large magnetic moment of the impurity atom, which undoubtedly indicates a strong change in the structure of the outer shell of the manganese under the influence of the interaction between the impurity and the matrix. It is quite probable that other anomalies mentioned at the start of the article (Mo, Re) are connected with similar effects. Such deviations should be expected also in all those cases when the impurity atom has the "proper" magnetic moment of the outer shell (Fe, Co).

Relation (2) allows us to predict the magnitude and sign of the field at the nuclei of elements for which there are no experimental data as yet. Thus, for alkali and alkali-earth metals, large positive fields should be observed. For elements of period VI, a jumplike change in the field should be expected from La to Hf, inasmuch as for Hf the filled shells contain 14 electrons more than for La. Great interest attaches to measurements of the fields at the nuclei of noble gases; these fields should also be large and positive. The field for xenon was measured in[8], but the sign of the field was not determined. To check whether the laws considered here are general, it is necessary to have also data for the elements of period II and III, which unfortunately are practically nonexistent.

The calculations of Watson and Freeman[9] have shown that the magnetic fields at nuclei of atoms having a proper magnetic moment (Mn, Fe, Co, Ni) are determined by the polarization of the electrons of the internal shells. Our results allow us to propose that the role of the internal shells is decisive also for atoms which have no magnetic moment. Regardless of the correctness of the model proposed by us, this conclusion is a direct consequence of the empirical laws considered above.

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