MAGNETIC RESONANCE IN RHOMBOHEDRAL WEAK FERROMAGNETICS

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On the basis of Dzyaloshinskiĭ's ideas on the nature of weak ferromagnetism, resonance frequencies are calculated for rhombohedral weak ferromagnetic crystals of the α-Fe_2O_3 and $MnCO_3$ type. Account is taken of the effect on the resonance of anisotropy in the basal plane, and the dependence of the resonance frequencies on the magnitude and direction of the magnetizing field is obtained. The theoretical formulas are compared with experimental data on α-Fe_2O_3.

1. Magnetic resonance is the most direct method of studying the energy spectrum of magnetic crystals. The peculiarities of the energy spectrum of weak ferromagnetics, which result from the peculiar nature of weak ferromagnetism as a property of antiferromagnetic crystals conditional on a definite symmetry, are most evident in the conditions of magnetic resonance, and especially in the form of the dependence of the resonance frequencies on the magnitude and direction of the magnetizing field. Therefore it is of interest to study the conditions of magnetic resonance in weak ferromagnetics by means of the Hamiltonian proposed by Dzyaloshinskiĭ[1] on the basis of symmetry considerations, and to compare the results obtained with the existing experimental data.

Since the only weak ferromagnetic for which there are experimental data on magnetic resonance, α-Fe_2O_3, belongs to the rhombohedral syngony, all our calculations will relate to crystals of this symmetry. Moreover the other best studied weak ferromagnetic, $MnCO_3$,[1,2] has a crystal lattice isomorphic with the α-Fe_2O_3 lattice.

The most complete experimental study of magnetic resonance in hematite was made by Kumagai et al.[3] In their work the dependence of resonance frequency on the magnitude and direction of the external field **H** was studied. In particular, it was shown that the usual Kittel resonance formula for a uniaxial ferromagnetic, with no account taken of anisotropy in the basal plane, agrees poorly with experimental data on the dependence of resonance frequency on the magnitude of a field **H** lying in the basal plane. Furthermore the experiment gave a very simple dependence of the magnitude of the resonance field $\mathbf{H}_\theta$ at a given frequency on the angle θ between the direction of this field and the trigonal axis [111] of the crystal:

$$H_\theta = H_\perp / \sin\theta, \tag{1}$$

where $H_\perp$ is the resonance field for $\theta = \pi/2$.

There has been only one attempt at a theoretical explanation of the experimental laws for resonance in hematite. This attempt, by Shimizu,[4] is based on old ideas about weak ferromagnetism, such as the explanation based on the presence in an α-Fe_2O_3 crystal of fine ferromagnetic impurities. For this impurity ferromagnetism, Shimizu included in the anisotropy energy terms through the sixth order; in consequence, by choice of the numerical values of the three anisotropy constants that appeared in the theory, he succeeded in giving a satisfactory explanation of the experimental data of Kumagai et al.[3] in the range of fields in which there is saturation. However, description of the resonance phenomenon in hematite on the basis indicated came into contradiction with static measurements of the magnetic properties of α-Fe_2O_3. In particular, it was found that the magnetic susceptibility in the direction of the trigonal axis should be appreciably larger than the susceptibility in the basal plane,* which was contrary to experiment.[5]

In the present work it will be shown that on the basis of the ideas developed by Dzyaloshinskiĭ on the nature of weak ferromagnetism, it is possible to give a more natural explanation of the observed resonance properties of hematite; furthermore,

*The susceptibility in the direction of the [111] axis should, according to Shimizu, be the resultant of the transverse antiferromagnetic susceptibility and of a susceptibility connected with rotation of the spontaneous magnetic moment of the ferromagnetic impurities.

this explanation is in good agreement with the static measurements of magnetization and susceptibility of these crystals.

2. We shall start with the following Hamiltonian, proposed by Dzyaloshinskii[1] on the basis of symmetry considerations for rhombohedral crystals of the α-Fe_2O_3 or $MnCO_3$ type:

$$\mathcal{H} = \tfrac{1}{2}Bm^2 + \tfrac{1}{2}bm_z^2 + \tfrac{1}{2}al_z^2 + q(l_xm_y - l_ym_x) + d(3l_x^2l_y - l_y^3)\,l_z + e(l_x^6 - l_y^6 - 15l_x^4l_y^2 + 15l_x^2l_y^4) - \mathbf{mh}. \quad (2)$$

Here the z axis is the trigonal axis, and the x axis is directed along one of the twofold axes in the (111) plane; $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/2M_0$, $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/2M_0$, where $\mathbf{M}_1$ and $\mathbf{M}_2$ are the sublattice magnetizations, for which, in accordance with the basic assumptions of spin-wave theory, the relations $\mathbf{M}_1^2 = \mathbf{M}_2^2 = M_0^2$ hold; or

$$l^2 + m^2 = 1, \qquad \mathbf{lm} = 0. \quad (3)$$

The parameters that appear in (2) have the following meanings: the exchange interaction parameter $B > 0$ leads to an antiferromagnetic arrangement of the sublattice magnetizations; the parameter $q > 0$ causes a disturbance of the strict antiparallelism of the vectors $\mathbf{M}_1$ and $\mathbf{M}_2$, so that a weak spontaneous moment $\mathbf{m} \perp \mathbf{l}$ appears; a and b are fourth- and sixth-order anisotropy constants, which for hematite satisfy the conditions*[1]

$$a > 0, \; e + d^2/4a > 0.$$

The last term in (2) represents the energy of the magnet in the external field $\mathbf{H} = \mathbf{h}/2M_0$. In the Hamiltonian (2) two fourth-order terms, not important for present purposes, have been omitted.

3. The spectrum of characteristic oscillations of the vectors $\mathbf{m}$ and $\mathbf{l}$ for rhombohedral weak ferromagnetics, with neglect of anisotropy in the basal plane (i.e., for $d = e = 0$), was calculated by Borovik-Romanov[2] and one of the authors[6,7] for the case in which the field H lies in the basal plane. We shall first generalize the results of these works to the case of arbitrary direction of H.

Let H make an angle θ with the [111] axis. Then, upon neglect of the c and d terms in (2) and upon supposing (without loss of generality) that H lies in the xz plane, it is easy to find, from the condition of minimum $\mathcal{H}$ with attention to (3), the following equilibrium values of $\mathbf{m}$ and $\mathbf{l}$ (for $h \ll B$):

*Under these conditions, in the equilibrium state (at H = 0) $\mathbf{m}$ is directed along one of the twofold axes in the basal plane, and $\mathbf{l}$ is in the vertical plane perpendicular to it and makes a small angle with the basal plane.

$$m_{x0} = (q + h\sin\theta)/B, \qquad m_{y0} = 0, \quad m_{z0} = h\cos\theta/(B+b),$$
$$l_{x0} = l_{z0} = 0, \qquad l_{y0} = l_0 = \sqrt{1 - m_0^2} \approx 1. \quad (4)$$

By considering, furthermore, small uniform oscillations of $\mathbf{m}$ and $\mathbf{l}$ about the values $\mathbf{m}_0$ and $\mathbf{l}_0$, we find in the usual way[8,9] the characteristic frequencies of these oscillations:

$$\omega_1 = (\gamma/2M_0)\sqrt{h\sin\theta\,(q + h\sin\theta)}, \quad (5)$$

$$\omega_2 = (\gamma/2M_0)\sqrt{Ba + q(q + h\sin\theta) + h^2\cos^2\theta}, \quad (6)$$

where $\gamma = ge/2mc$ is the magnetomechanical ratio (ω = angular frequency).

Oscillations of frequency ω_1 can be excited by radio waves of the centimeter range, and in fact they were observed in resonance experiments of Kumagai et al.[3] The second branch of the oscillations is related to much higher frequencies, of order 10^{12} to 10^{13} cps. Observation of it requires larger fields, $H \sim 10^4$ to 10^5 oe, and electromagnetic radiation of wavelength $\lambda \sim 10^{-1}$ to 10^{-2} cm.

Solution of the resonance formula (5) for the external field H gives the experimentally established relation (1), with

$$H_\perp = \sqrt{(H_D/2)^2 + (\omega_1/\gamma)^2} - H_D/2, \qquad H_D = q/2M_0. \quad (7)$$

Thus even without allowance for anisotropy in the basal plane, the theory explains well the observed dependence of the magnitude of the resonance field H on its direction in a plane passing through the trigonal axis. However, the theoretical relation (7) between the resonance field $H_\perp$ in the basal plane and the frequency ω_1 is poorly satisfied experimentally. Therefore, as has already been pointed out by Vonsovskiĭ and Turov,[7] here it is necessary to take account of anisotropy in the basal plane, described by the d and e terms in the Hamiltonian (2). This will be done below.

4. Let the field H lie in the (111) plane and make an angle φ with the x axis. Then from the minimum condition for the complete Hamiltonian (2) in the range of fields $h^* < h \ll B$, we find

$$\mathbf{m}_0 \parallel \mathbf{H}, \qquad m_0 = (q + h)/B, \qquad l_0 = \sqrt{1 - m_0^2} \approx 1, \quad (8)$$

$\mathbf{l}_0$ lies in the plane perpendicular to H and makes with the (111) plane an angle

$$\delta = (d/a)\cos 3\varphi. \quad (9)$$

The field h^* represents an effective anisotropy field in the basal plane; for $h > h^*$ saturation occurs, in the sense that $\mathbf{m}_0 \parallel \mathbf{H}$. Approximately,

$$h_1^* = 36B\,(e + d^2/4a)/q. \quad (10)$$

For hematite in particular, as will be clear from the estimates made below, $H^* = h^*/2M_0 \sim 10^2$ oe.

Knowing the equilibrium vectors $\mathbf{m}_0$ and $\boldsymbol{l}_0$, we can calculate anew the spectrum of oscillations of the system about this equilibrium state. A very laborious calculation on the basis of the complete Hamiltonian (2), with attention to the relations (8) and (9), leads to the following two characteristic frequencies of oscillation for this case:

$$\omega_1 = (\gamma / 2M_0) \sqrt{h(h+q) + 36B(e + d^2/4a)\cos 6\varphi}\,. \quad (11)$$

$$\omega_2 = (\gamma / 2M_0) \sqrt{Ba + q(q+h) + 9Bd + 6Be\cos 6\varphi}\,, \quad (12)$$

As is clear from (12), the fourth- and sixth-order anisotropy is practically without effect on the second resonance frequency, since the d and e terms that occur in it are always small in comparison with the term Ba. On the contrary, for the first resonance frequency ω_1 the role of anisotropy in the basal plane can be appreciable if the field **H** is not very large. The range of fields in which there is an effect of anisotropy of higher than second order is, as a rule, appreciably larger for the weakly ferromagnetic crystals under consideration than for ordinary ferromagnetics of the same symmetry, since in the present case the role of "anisotropy constants" is played not by the parameters d and e themselves, but by quantities proportional to the geometric mean of $e + d^2/4a$ and of the exchange parameter B. Consequently, in this respect weak ferromagnetics are similar to ordinary antiferromagnetics.

5. We now show under what conditions the oscillations of frequencies ω_1 and ω_2 are excited. For this purpose we find the susceptibility of a weak ferromagnetic with respect to a high-frequency magnetic field $\mathbf{h}_\omega$; we start with the equation of motion for the magnetic moments $\mathbf{M}_1$ and $\mathbf{M}_2$ of the sublattices:

$$d\mathbf{M}_j/dt = \gamma[\mathbf{M}_j \times \mathbf{H}_j], \qquad j = 1, 2. \quad (13)$$

Here the effective fields $\mathbf{H}_j$ acting on the sublattices are found from the Hamiltonian (2) and the relation $\mathbf{H}_j = -\partial\mathcal{H}/\partial\mathbf{M}_j$. We shall consider that the external field consists of a constant field $H = H_x$, directed along the x axis in the basal plane, and of a high-frequency alternating field $\mathbf{h}_\omega$, whose amplitude is small in comparison with H_x. A standard calculation gives the following expression for the high-frequency tensor susceptibility:

$$\chi_{\alpha\beta} = \begin{vmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & \chi_{yz} \\ 0 & \chi_{zy} & \chi_{zz} \end{vmatrix}, \qquad \chi_{xx} = \chi_0\omega_2^2/(\omega_2^2 - \omega^2),$$

$$\chi_{yy} = (M_x/H_x)\omega_1^2/(\omega_1^2 - \omega^2), \qquad \chi_{zz} = \chi_0\omega_1^2/(\omega_1^2 - \omega^2),$$

$$\chi_{yz} = -\chi_{zy} = i\chi_0(\omega/\gamma H)\,\omega_1^2/(\omega_1^2 - \omega^2),$$

$$M_x = \chi_0(H_D + H), \quad \chi_0 = 4M_0^2/B.$$

From the formulas presented it is evident that the oscillations of frequency ω_1 are excited when the high-frequency field is perpendicular to the constant field, and the oscillations of frequency ω_2 when it is parallel to it. The presence of nondiagonal elements of the tensor $\chi_{\alpha\beta}$ shows that there is gyrotropy in the medium.

It is possible to allow for a damping term in equation (13), for example in the form proposed by Landau and Lifshitz;[10] this was done for ordinary antiferromagnetics by Kaganov and Tsukernik[11] and also by Seĭdov.[12] If the width $\Delta\omega$ of the resonance line is then determined from the expressions obtained for $\chi_{\alpha\beta} = \chi'_{\alpha\beta} - i\chi''_{\alpha\beta}$, it turns out that in weak ferromagnetics, just as in antiferromagnetics,[11] $\Delta\omega$ is connected with the dimensionless damping parameter α of the Landau-Lifshitz equation of motion by the following relation: $\Delta\omega \approx \alpha\omega_E$ ($\omega_E = \gamma B/2M_0$ is the so-called exchange frequency).

We remark that the analogous relation for ordinary ferromagnetics has the form $\Delta\omega \approx \gamma\omega_0$, where ω_0 is the resonance frequency.[13] Consequently, if the parameter α in antiferromagnetics (and in weak ferromagnetics) had the same nature and the same order of magnitude as in ferromagnetics, then $\Delta\omega$ would be about three orders of magnitude larger in the former than in the latter. However, no great differences are observed between the line widths for antiferromagnetics and for ferromagnetics. Apparently the question of the formal description of relaxation terms in the equations of motion for antiferromagnetics and weak ferromagnetics, and also of the nature of the line widths in them, needs to be subjected to a special and more detailed study.*

6. We apply the theoretical results obtained to the discussion of the resonance properties of hematite.[3] It has already been indicated that the theory explains well the experimentally established formula (1) for the dependence of the magnitude of the resonance field on its direction in a plane passing through the [111] axis. Kumagai et al.[3] also investigated the relation between the frequency ω_1 and a resonance field H lying in the basal plane. We rewrite formula (11), which should describe this relation, in the following form:

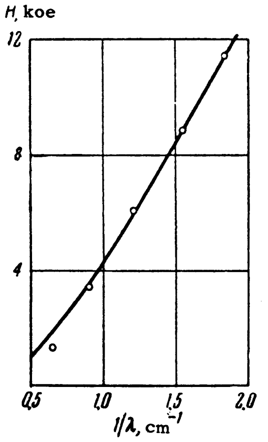
$$\omega_1/\gamma = \sqrt{H(H + H_D) + H_\Delta^2\cos 6\varphi},$$

$$H_\Delta^2 = 36B(e + d^2/4a)/4M_0^2. \quad (14)$$

Thus in the resonance formula (14) there occur two unknown parameters† H_Δ and H_D. The first

*Cf. also the work of Dayhoff.[14]

†If we do not include the g factor; this we set equal to 2.



of these can be estimated from the angular dependence of the resonance field (i.e., the dependence of H on φ for given frequency ω_1), observed by Anderson et al.[15] and less precisely by Kumagai et al.[3] This estimate gives approximately $H_\Delta = 1450$ oe. A value of the parameter H_D was selected by the criterion of best fit between theory and experiment for the dependence of ω_1 on H. The figure shows the theoretical curve for the relation between $1/\lambda = \omega_1/2\pi c$ and a resonance field H directed along the "easy axis" x [this corresponds to $\cos 6\varphi = 1$ in formula (14)], for $H_D = 22{,}800$ oe. The experimental data[3] are plotted as points. As is evident from the figure, there is completely satisfactory agreement between theory and experiment except in the low-field range. This was likewise the case in the work of Shimizu.[4] Presumably, because of various crystal defects, the saturation of the magnetization assumed by us is not present at fields $\lesssim 2000$ oe. In fact, from magnetization curves of hematite taken by other authors[16] it is clear that saturation in the basal plane is not attained at field strengths below 1000 to 2000 oe, whereas according to (10) saturation should occur for an ideal crystal at fields

$$H \sim H^* = H_\Delta^2 / H_{\text{Д}} \sim 100 \text{ oe}.$$

The important superiority of our theory is that, in contrast to the theory of Shimizu, it leads to good agreement of the resonance experiments with the results of static measurements of the spontaneous magnetization M_S and of the transverse antiferromagnetic susceptibility χ of hematite. The fact is that from the statistics of the measurements it is possible to determine in an independent way the field H_D responsible for the weak ferromagnetism,[1,6] since $H_D = M_S/\gamma$. According to data of Néel and Pauthenet,[5] at room temperature $M_S \approx 0.4$ cgs emu and $\chi = 2 \times 10^5$; consequently $H_D \approx 2 \times 10^4$ oe, which is very close to the value $H_D = 22{,}800$ oe found above from resonance measurements.*

For more detailed comparison of theory with experiment and for resolution of the still remaining difficulties in the low-field range, it is necessary to carry out experimental studies of both the magnetic and the resonance properties of hematite (or $MnCO_3$) on the same monocrystalline specimens.

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*This agreement can be improved further by taking for the g factor a value slightly greater than 2.