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SPIN DENSITY OF THE CANTED MOMENT IN α-Fe₂O₃

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Résumé. — La densité de spin de la composante ferromagnétique du moment non colinéaire dans l’haematite a été mesurée avec des neutrons polarisés. On trouve que cette densité diffère de celle de l’ion Fe³⁺.

Abstract. — The spin density ferromagnetic component of the canted moment in hematite was measured with polarized neutrons and found to differ from that of the Fe³⁺ ion.

Introduction. — It has been proposed by Dzyaloshinski [1] that the small residual ferromagnetism in hematite (α-Fe₂O₃) has its origin in a canting of the antiferromagnetic sublattices. Magnetic measurements [2] have established that this moment (approximately 0.4 emu/gm) exists above a transition temperature of 250 °K, and is confined to the rhombohedral (111) plane. The basic antiferromagnetic structure, as established by the original neutron diffraction measurements [3], consists of the Fe³⁺ spins in each (111) plane being parallel, with alternating planes being antiparallel (fig. 1); these measurements also demonstrate that above the 250 °K transition the spins lie within the (111) plane, and that the transition corresponds to a change of spin direction to along the trigonal axis. On the basis of the symmetry of these two phases, Dzyaloshinski concluded that in the high temperature phase the spins were allowed to cant toward each other within the plane, but the canting was not allowed by the symmetry when the spins are along [111]. The physical origin of the canting was later attributed by Moriya [4] to the anisotropic superexchange interaction.

The antiferromagnetic structure depicted in figure 1 gives rise to extra magnetic scattering for reflections with \((h + k + l)\) odd. If canting is present there will also be a contribution to the reflections with \((h + k + l)\) even, whose intensity will be proportional to the square of the magnitude of the ferromagnetic component of the moment. In the present investigation we describe an attempt to observe this contribution using polarized neutron scattering.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

Experimental. — For neutrons polarized parallel or antiparallel to an external field on a ferromagnetic crystal, whose spins are along the field, we
can define for a reflection whose scattering vector is perpendicular to the polarization direction the so-called polarization ratio,

\[ R = \frac{I_+}{I_-} = \frac{(N + M)^2}{(N - M)^2}, \]

which is the ratio of the reflected intensities when the incident neutrons are parallel (+) and antiparallel (−) to the external field [5]. Here \( N \) is the nuclear and \( M \) the magnetic structure factor of the scattering plane. The observed ratio can be solved for the ratio \( \gamma = M/N \), so that if the crystal structure (and thus \( N \)) is known, \( M \) can be determined. \( M \) is proportional to a geometric structure factor and also to \( \mu f \), where \( \mu \) is the total value of the moment, as measured by the magnetization, and \( f \) is the form factor, whose angular dependence is the Fourier transform of the spatial distribution of the scattering spin density.

In practice, the number of reflections accessible to measurement in this instance are severely limited by two factors. First is the extreme smallness of the ratio \( \gamma \). Considering the available neutron flux and other experimental factors, it is difficult to measure \( R \) to much greater precision than \( 10^{-3} \); therefore since

\[ R = \frac{(1 + \gamma)^2}{(1 - \gamma)^2} \approx 1 + 4\gamma \quad (\gamma \ll 1), \]

\( \gamma \) cannot be measured accurately if it is less than about \( 2.5 \times 10^{-4} \). In the present case this fact limits the choice to reflections whose nuclear structure factors are small, a condition occurring only when the separate contributions of Fe and O are of opposite sign. Secondly, in the ferromagnetic reflections there is also a contribution from the covalent spin density of the antiferromagnetic component. Due to the lack of translational symmetry of the iron atoms in the two antiparallel sublattices, there can be a contribution to normally “forbidden” reflections just as the bonding electron density in diamond gives rise to forbidden x-ray reflections. This effect was observed [6] for magnetic scattering in MnF₂. To eliminate this contamination in measuring the ferromagnetic component, it is necessary to align the ferromagnetic component completely along the field so that the antiferromagnetic component is perpendicular to the neutron polarization and does not contribute significantly to \( R \). This condition suggests reflections in zones that lie within the (111) plane.

Results and discussion. — As a result of these restrictions only four reflections are suitable. The results of the measurement of the ratio \( \gamma \) and the magnetic structure factor \( M \) are listed in the following table.

<table>
<thead>
<tr>
<th>hkl</th>
<th>( \sin \theta/\lambda )</th>
<th>( \gamma )</th>
<th>( M_{\text{obs}} ) ((10^{-14} \text{ cm}))</th>
<th>( M_{\text{calc}} ) ((10^{-14} \text{ cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>002</td>
<td>.240</td>
<td>+.0010 ( \pm .0004 )</td>
<td>( -.011 \pm .004 )</td>
<td>( -.064 )</td>
</tr>
<tr>
<td>222</td>
<td>.217</td>
<td>-.0025 ( \pm .0002 )</td>
<td>( +.213 \pm .020 )</td>
<td>( +.210 )</td>
</tr>
<tr>
<td>114</td>
<td>.407</td>
<td>-.0003 ( \pm .0005 )</td>
<td>( +.005 \pm .008 )</td>
<td>( +.076 )</td>
</tr>
<tr>
<td>330</td>
<td>.407</td>
<td>-.0045 ( \pm .0004 )</td>
<td>( +.082 \pm .007 )</td>
<td>( +.076 )</td>
</tr>
</tbody>
</table>

In the final column of the table are listed the values of \( M \) calculated on the basis of the observed moment and the form factor of Fe³⁺ that was found to match the antiferromagnetic intensities measured on a powdered hematite sample [7]. To scale \( M \) we used nuclear structure factors calculated with parameters obtained from a recent single crystal refinement [8]. The measurements were performed on a synthetic crystal and checked for extinction and double Bragg scattering.

There are obvious discrepancies between the expected and observed values. Of particular interest is the observed difference between (114) and (330), which are equivalent in the space group of hematite \((R\bar{3}c)\) for the special positions that the Fe atoms occupy. We are thus led to the conclusion that the ferromagnetic spin density is not centered on the Fe atom positions. Examination of the structure factor expressions for \( R\bar{3}c \) shows that only the general position destroys the above mentioned equivalence. This puts rather severe
restrictions on the possible location of the ferromagnetic spin density; for instance, it cannot lie along, or be symmetrically disposed about, the Fe-O bonds. A model was found that gives good agreement with the observations, although it is not necessarily unique. In this model isolated spherical distributions of magnetic charge, with a mean radius roughly of 0.25 Å, are placed about 0.5 Å away from each Fe atom on the line joining the atoms to each of the nearest neighbor Fe atoms within the (111) plane. The agreement of the observations with the magnetic structure factors, calculated as a function of a parameter relating to the displacement of the charge distribution from the Fe atom positions, is shown in figure 2.

Irrespective of the model chosen, the data described above clearly indicate the ferromagnetic spin density is distributed in space differently from the antiferromagnetic spin density. This may be restated by saying that the spin density distribution in this compound is a vector rather than a scalar function, and to be specified completely must be given a direction as well as a magnitude at every point in space. It has been pointed out recently by Blume [9] that if orbital moment is included in calculation of neutron scattering, the form factor should in general be expressed as a scalar function, and to be specified completely must be given a direction as well as a magnitude at every point in space. In this sense, since the anisotropic superexchange arises only because of the very slight departure from spherical symmetry, with the consequent admixing of orbital moment, the present observations may constitute a special case of a rather general phenomenon.

Discussion

Dr Bertaut. — 1° Le couplage antisymétrique de Dzialoshinski-Moriya est dû au couplage spin-orbite et à l'échange de sorte que les mêmes électrons participent à l'échange antiferromagnétique et au couplage D. M. Pourquoi leur densité serait-elle différente ?

2° On a montré (Trammel, Saint James) que les facteurs de forme magnétique sont différents pour le spin et pour l'orbite. Avez-vous pris les mêmes facteurs et est-ce qu'une éventuelle différence influerait sur votre résultat ?

3° Si le champ appliqué est dans le plan (111), on a selon Paunzenet, \( \sigma = \sigma_0 + \gamma H \). Est-ce que le terme \( \gamma H \) influe sur le résultat ?

Dr Pickart. — 1° J'ai moi-même posé la question à de nombreuses personnes et n'ai pas reçu de bonne réponse. Naturellement, nous considérerons les mêmes électrons. Ce que nous affirmons c'est que le spin, dans le cas ferromagnétique, se trouve dans une position différente de celle du cas antiferromagnétique. Il est probable que c'est le couplage spin-orbite qui est en quelques manière la cause de ce phénomène. Nous étudions actuellement \( \text{YFeO}_3 \), qui possède aussi un moment non linéaire (même plus grand) pour voir si le phénomène est général.

2° La vraie valeur du moment orbital considéré ici est tout à fait faible. L'écart observé est beaucoup plus grand que la différence entre le facteur de forme de l'ion Fe\(^{3+}\) et celui tenant compte du moment orbital.

3° Oui. Les mesures quantitatives données ici ont été faites à 5 000 Oe. Nous avons bien examiné qualitativement la paire (330) (114) à 1 000 Oe et avons trouvé le même écart.

Dr Abrahams. — L'équivalence des réflexions (114) et (331) rhomboédriques n'est pas nécessairement maintenue dans la symétrie plus basse du groupe d'espace de Shubnikov nécessitée par la perte de l'axe trigonal (due au spin perpendiculaire à (111)). Avez-vous envisagé les conséquences du groupe de Shubnikov sur les valeurs attendues de \( M_{\text{calc.}} \) ?

Dr Pickart. — Non ! En l'absence de preuve contraire aux rayons X, nous prenons les paramètres donnés par Zoltai pour \( R \text{ 3c} \). Une déformation vers une symétrie plus basse avec variation de paramètres pourrait donner les mêmes résultats que ceux que nous observons. Je répète qu'il n'y a aucune évidence de déformation.

Pr Opechowski. — Des positions équivalentes dans un groupe spatial ne sont pas en général équivalentes dans un groupe de Shubnikov appartenant à la famille du groupe spatial considéré. C'est, à mon avis, une autre manière de formuler la remarque du Dr Abraham.

Dr Pickart. — Je suis d'accord.

REFERENCES