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Low-energy magnetic excitations in wustite ($Fe_{1-x}O$)

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Magnetic-excitation dispersion curves of wustite ($Fe_{1-x}O$) have been measured at liquid-helium temperature by inelastic neutron scattering in the usual symmetry directions of reciprocal space. The experimental dispersion curves are interpreted by a Heisenberg spin-wave model with exchange integrals extended to second neighbors. An uniaxial crystal-field anisotropy parameter is evaluated in accordance with theoretical calculations of Kanamori. The first- and second-neighbor exchange integrals, as well as some general magnetic properties are calculated.

I. INTRODUCTION

The iron monoxide $Fe_{1-x}O$, also called wustite, belongs to the group of antiferromagnetic monoxides (like MnO, NiO, and CoO) with rocksalt structure in the paramagnetic phase. The antiferromagnetic properties of MnO and NiO are well understood, and magnons of these materials have been studied by inelastic neutron scattering[1,2] Raman light scattering,[3] and infrared spectroscopy.[4,5] The results of these measurements can be interpreted in terms of Heisenberg models with first- and second-neighbor exchange integrals. The magnetic anisotropy mainly consists of magnetic dipolar interactions between spins. Such an explanation is due to the fact that the ground states of Mn^{2+} and Ni^{2+} ions are orbital singlet states, respectively Γ_1 with zero orbital momentum and Γ_2 with quenched orbital momentum. Because the orbital angular momentum of Co^{2+} and Fe^{2+} ions is not quenched by the crystal field, cobaltous and iron oxides exhibit features which are different from those of the two other materials. Indeed, the ground states of Co^{2+} and Fe^{2+} ions are orbital triplet states, the orbital angular momentum giving rise to the possibility for existence of spin-orbit coupling, crystal field, and exchange effects. So, the magnetic anisotropy of FeO has not the same origin as in MnO and NiO.[6] Cobaltous monoxide has been studied by neutron techniques[7] and light scattering,[8,9] as well as antiferromagnetic resonance in the infrared.[10,11] Nevertheless, there remain unsolved problems with respect to magnetic excitation properties. Since no experimental data are available for FeO, the study of the magnon dispersion curves was necessary to complete the monoxides series. This investigation follows phonon dispersion-curve measurements on the same compound recently published by the authors.[12]

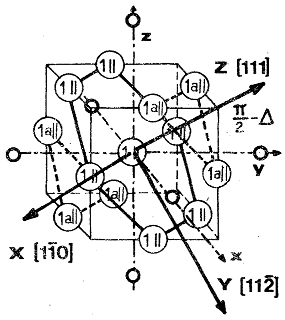
In Sec. II some generalities like structure, electronic properties, and anisotropy are reviewed. The experimental results are reported in Sec. III. A simple phenomenological spin-wave theory is proposed in Sec. IV, completed by a discussion pointing out unsolved problems in our study.

II. GENERALITIES

Above the Néel temperature $T_N \simeq 198$ °K, the FeO crystal has the cubic NaCl structure with a space group $Fm3m$ (O_h^5). Below T_N, the compound becomes antiferromagnetic of type II,[13] the phase transition being accompanied by a lattice distortion.[14,15] The deformation consists of an elongation along the $\langle 111\rangle$ axis and is due to magnetostriction effects.[6] According to Roth,[14] the spins are arranged in ferromagnetic sheets parallel to (111) planes and reverse from one plane to the next. The magnetic group of FeO is the rhombohedral $R_I\bar{3}c$ one and belongs to the $\bar{3}2/m1'$ class of order 24. Because of the different spin orientation, MnO, NiO, and CoO belong to the monoclinic C_c2/c magnetic space group.

Below T_N, the distortion reduces the distance between parallel spin ions and increases that between antiparallel spin ions. Such a difference has an influence on the exchange integrals, which must be distinguished in $J_1^{\parallel}$ and $J_1^{a\parallel}$, for parallel and antiparallel spin first neighbors, respectively. We expect $J_1^{\parallel}$ to be stronger than $J_1^{a\parallel}$ (Fig. 1).

The symmetry of the spin structure allows four equivalent $\langle 111\rangle$ magnetization axes, so the crystal will usually contain four distinct magnetic domains. Consequently, the reciprocal space must



NEIGHBORS			
TYPE	1^{ST}		2^{ND}
INDEX	1		2
NUMBER	12		6
SPIN	6 ↑	6 ↓	6 ↓
SYMBOL	1‖	1a‖	○
EXCHANGE INTEGRAL	$J_1^{\parallel}$	$J_1^{a\parallel}$	J_2
DISTORTION	$-\delta$	$+\delta$	0
$\delta=\frac{a\Delta}{2\sqrt{2}}$	$a \cong 4.30$ Å		

FIG. 1. Neighboring ions and exchange integrals. An Fe^{2+} ion with spin up is represented with its first and second metallic neighbors. The coordinate systems are represented. The attached table gives some general information on the structure.

be considered as a superposition of four spaces. In Fig. 2 we represent a (0$\bar{1}$1) plane of the reciprocal space of the lattice with zone boundaries of spaces of [111],[$\bar{1}$11],[1$\bar{1}$1], and [11$\bar{1}$] magnetization domains.

It is useful to consider the electronic structure of the Fe^{2+} ion in the crystal; the ground state of the free ion is a $^5D_4$ spectral term with total angular momentum $L=2$ and total spin $S=2$. In the wustite crystal, the ion is influenced by the following perturbations: a cubic crystal field of octahedral symmetry, the spin-orbit coupling, a trigonal crystal field due to the distortion at magnetic ordering, and an exchange field in the antiferromagnetic phase.

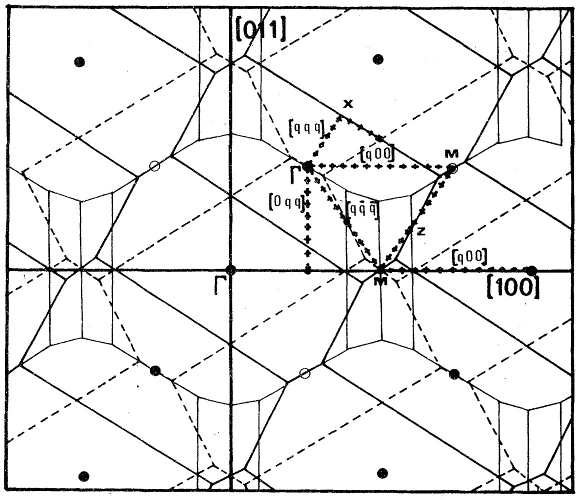


FIG. 2. Multidomain crystal scattering plane. The superposition of the four-domains reciprocal spaces occuring in the crystal is given with the following lines: —, [111] magnetization axis; ---, [$\bar{1}$11] magnetization axis; —, [1$\bar{1}$1] and [11$\bar{1}$] magnetization axes. The crosses represent the direction of measurements and are labeled for the [111] domain.

The $^5D_4$ orbital ground state is fivefold degenerate for a total degeneracy of 25. This state is split by the octahedral crystal field into two levels; the lowest one is an orbital triplet state Γ_5 with total degeneracy of 15 and the highest one is an orbital doublet Γ_3 (total degeneracy 10). Only the ground state needs to be considered, the splitting of about 10^4 cm^{-1} being beyond the energy range accessible to neutron scattering. The Γ_5 triplet has the same symmetry as a manifold of p states with an effective orbital momentum $l=1$. The treatment of the perturbations listed above is a quite complicated problem. Indeed, these contributions have such magnitudes that the splitting of the Γ_5 level is accompanied by mixing of levels. Clearly, these perturbations must be treated simultaneously in order to know the accurate single-ion electronic structure. Since our experimental results concern only the lowest excitation branch, (the so-called magnon branch), we do not perform such a calculation. Nevertheless, a complete analysis of the magnetic excitations await these theoretical developments compared with experimental higher-energy branches.

III. EXPERIMENTS AND RESULTS

The crystal employed in our experiments was prepared by a floating-zone technique using an image furnace. The method of preparation and growth has been already described.[12] The specimen consists in a black-colored cylindrical crystal of about 1.5 cm^3 with a stoichiometric ratio x estimated about 0.07. Neutron-elastic-Bragg scattering reveals a [100] axis nearly localized along the cylinder axis. The diffraction spectrum clearly shows the existence of two main monocrystals slightly disoriented with about the same scattering intensity, as well as some smaller parasitic crystals. The experiments have been performed at liquid-helium temperature using the triple-axis spectrometer H_4 on the $EL3$ reactor of CEN Saclay and the triple-axis spectrometer $IN1$ at the Institut Laue-Langevin of Grenoble.

The crystal was oriented with a [0$\bar{1}$1] axis normal to the horizontal scattering plane. The measurements have been done in the principal high symmetry directions along the paths reported in Fig. 2. The labeling of these directions is relative to a [111]-magnetization-axis domain.

The polydomain character of the crystal (Fig.2) gives rise to ambiguity in assigning energy to wave vectors. To remove the ambiguity as far as possible, we proceeded in the following ways: the results were checked in complementary directions, for example, several points were measured in two

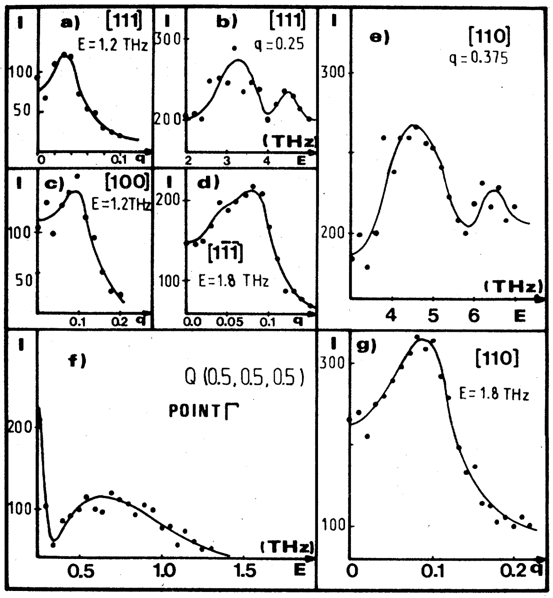


FIG. 3. Magnon groups measured in wustite. Some magnetic excitation groups are given. The intensity of counting I is in arbitrary units. The direction of propagation, energy, and wave vector of the magnon are specified.

[q00] equivalent directions represented in Fig. 2. Starting with unambiguous points, we used the continuity of the branches for new measurements. These checks were compared with inelastic neutron scattering cross-section calculations based on our model explained in Sec. IV.

Nevertheless, because of the poor quality of the sample, the labeling of the results could not always be ascertained; such points were systematically rejected. Some typical neutron groups are shown in Fig. 3. The results of our measurements, corrected for resolution and crystal quality effects, are plotted in Fig. 4.

The following remarks may be made: (i) As seen in Fig. 3f, the lowest energy at Γ point of the magnetic Brillouin zone is not equal to zero, but there is a small gap of about 0.75 THz (25 cm^{-1}): (ii) In any direction the observed neutron groups give indication of a very flat branch, the magnetic character of which was confirmed by measurements at room temperature. No magnetic scattered intensity could be observed around 6 THz; (iii) In contrast with MnO and NiO, the magnon energies in the [111] direction are not high.

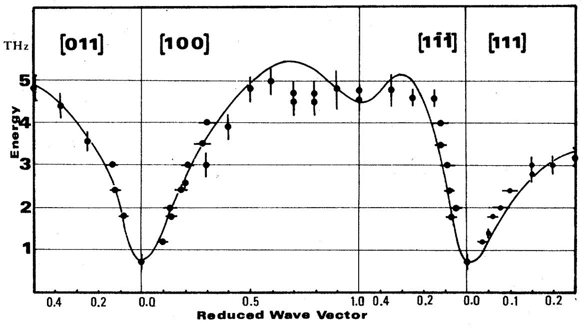


FIG. 4. Magnetic excitation dispersion curves in wustite. The full lines are the theoretical curves obtained with the model.

IV. THEORETICAL INTERPRETATION AND DISCUSSION

A. Theory

Our measurements concern only the first branch; hence our interpretation is made with a phenomenological spin-wave model based on a Heisenberg Hamiltonian with anisotropic contribution, the spin Hamiltonian acting within the Γ_5 ground state. This spin Hamiltonian is written

$$H = H_{ex} + H_{anis} . \tag{1}$$

The exchange Hamiltonian is the well-known Heisenberg-Dirac Hamiltonian

$$H_{ex} = \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j \tag{2}$$

taking the form

$$H_{ex} = \sum_{i,i'} J_1^{\parallel} \vec{S}_i \cdot \vec{S}_j + \sum_{j,j'} J_1^{\parallel} \vec{S}_j \cdot \vec{S}_{j'} + \sum_{i,j} J_1^{a\parallel} \vec{S}_i \cdot \vec{S}_j + \sum_{i,j} J_2 \vec{S}_i \cdot \vec{S}_j , \tag{3}$$

if extended to second metallic neighbors. The first terms of Eq. (3) are summations over pairs of nearest neighbors in one (i, i') or the other (j, j') sublattice. $J_1^{\parallel}$ is the parallel spin exchange integral. The third term is a sum over pairs of nearest-neighbor spins belonging to different sublattices with $J_1^{a\parallel}$ exchange integral. The last term is a sum over next-nearest neighbors with J_2 exchange integral. It should be noted that the exchanges are in fact superexchanges involving an intermediate O^{2-} ion with Fe^{2+}–O^{2-}–Fe^{2+} paths at 90° for J_1 and at 180° for J_2. Theoretical calculations of Anderson[16] predict J_2 stronger than J_1.

The anisotropy Hamiltonian H_{anis} can be given in terms of a single-ion Hamiltonian. By restricting ourselves to the uniaxial terms given by J. Kanamori,[6] expressed with new coordinates attached to the spin system (Fig. 1), we obtain

$$H_{anis} = (3/2S^2) T (S_i^z)^2 = D (S_i^z)^2 , \tag{4}$$

where T is the anisotropy parameter given by Kanamori.

The eigenvalues of the spin Hamiltonian are obtained by applying the standard Holstein-Primakoff transformation method[17] and can be expressed

$$E(\vec{q}) = 2nS[(A(\vec{q}) - D/n)^2 - B^2(\vec{q})]^{1/2}, \tag{5}$$

where n is the number of equivalent neighbors ($n = 6$) and S is the total spin number in Γ_5 ($S = 2$).

The functions $A(q)$ and $B(q)$ can be expressed

$$\begin{aligned} A(\vec{q}) &= J_1^{\parallel}[V_1^{\parallel}(\vec{q}) - 1] + J_1^{a\parallel} + J_2, \\ B(\vec{q}) &= J_1^{a\parallel} V_1^{a\parallel}(\vec{q}) + J_2 V_2(\vec{q}), \end{aligned} \tag{6}$$

where $V(\vec{q})$ are summations over equivalent neighbors of the general form

$$V(\vec{q}) = \frac{1}{n} \sum_{r_i - r_j} e^{j\vec{q}\cdot(\vec{r}_i - \vec{r}_j)}, \tag{7}$$

$\vec{q}$ being the wave vector.

B. Model calculations

The model was fitted to the results for the magnon branch in the three directions [100], [111], and [1$\bar{1}\bar{1}$] by use of a nonlinear least-squares routine. The resulting parameters are

$$\begin{aligned} &J_1^{\parallel} = -3.70\ \mathrm{cm}^{-1}, \quad J_1^{a\parallel} = -2.06\ \mathrm{cm}^{-1}, \\ &J_2 = 6.52\ \mathrm{cm}^{-1}, \quad D = -0.68\ \mathrm{cm}^{-1}. \end{aligned} \tag{8}$$

The corresponding calculated dispersion curves are reported together with experimental data in Fig. 4. Compared with known values,[6] the magnitudes of the exchange integrals are quite satisfactory. The axial-field anisotropy constant D of -0.68 cm^{-1} implies, in conformity with Eq. (4), the value -1.8 cm^{-1} for T; this nearly agrees with Kanamori's theoretical value of -1.5 cm^{-1}. Considering the dispersion curves, it may be seen that the agreement is reasonable, though we have some difficulties to reproduce the very flat character of the branch in the [100] direction.

C. Discussion

As pointed out by Kanamori,[6] anisotropy terms of nonaxial origin, removing the degeneracy of the spin modes, are expected to be important. Unfortunately, the results obtained near the zone center are too ambiguous to give a credible value. Some scans, for instance, those represented in Fig. 5(b), suggest the existence of a second branch. But because of the poor crystal quality, this point could not be confirmed. On the other hand, we observed a broad neutron group at the point (1, 1, 1) [Fig. 5(a)], which is a Γ point in all the domains (Fig. 2). Since the magnetic character of the group could not be checked, we cannot clearly identify this group as a higher branch. Furthermore, since the phonon frequency distribution has a peak at 4.5 THz,[12] the group [Fig. 5(a)] may derive from incoherent nuclear scattering.

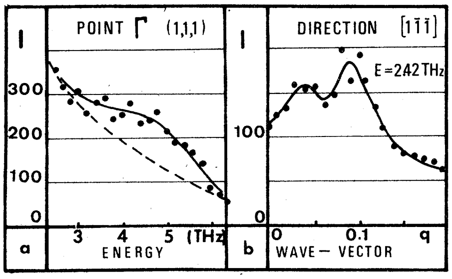


FIG. 5. Two puzzling neutron groups in wustite. Group (a) corresponds to a measurement at a Γ point. Group (b) reveals a weak splitting of the magnetic branch. I is the counted intensity.

A striking feature of our calculations is related to the ferromagnetic character of the nearest-neighbor exchange integrals. This fact is at the origin of some problems concerning the calculated magnetic properties. Indeed, the application of the molecular-field theory on evaluating the Néel (T_N) and paramagnetic Curie-Weiss temperature (Θ_c), gives results in bad agreement with known values. Our set of parameters leads to a T_N of 225 °K and to a Θ_c of -23 °K. Experiments[18,19] give a Néel temperature of 198 °K. The paramagnetic Curie-Weiss temperature for FeO is subject to discussion, and values in the literature are -570,[20] -190,[21] and -135 °K.[19] Using the magnetic susceptibility measured by Bizette[20] ($\chi_{T_N} = 8 \times 10^{-3}$ emu/*mole*), the paramagnetic Curie-Weiss law becomes

$$\chi(T) = 2.0/(T + 23). \tag{9}$$

The ferromagnetic character of J_1 is in our spin-wave model mainly related to the low-energetic magnons in the [111] direction. The TA phonons[12] have comparable energy, and the possibility of interactions between spins and lattice is not excluded. Nevertheless, experiments as a function of temperature show that the excitations measured in that region are of magnetic character.

Another point is the important splitting of J_1 into $J_1^{\parallel}$ and $J_1^{a\parallel}$. By neglecting the isotropic contraction due to the decreasing of the temperature, the exchange interaction can be written following Morosin[22]

$$\begin{aligned} J_1^{\parallel} &= J_1(1 + \tfrac{1}{2}\epsilon\Delta), \\ J_1^{a\parallel} &= J_1(1 - \tfrac{1}{2}\epsilon\Delta), \end{aligned} \tag{10}$$

where

$$\epsilon = r\frac{\partial \ln T_1}{\partial r}$$

and r is the distance between iron ions. With $J_1^{\parallel}$

and $J_1^{a\parallel}$, respectively, equal to the values obtained in our model, and by taking into account the experimental distortion angle,[6,15] we have ϵ equal to about 65, which is to be compared to the value found in MnO and MgO ($\epsilon = 20$).[22,23] This outlines the great sensitivity of the exchange integral to the interionic distance, and may partly explain the high influence of the stoichiometry on the magnetic properties.

So our simple phenomenological model gives satisfactory results. Nevertheless, these calculations are valid only for the first branch which reveals little of the relative magnitudes of the various contributions listed in Sec. II. In order to have a more complete theory, it would be necessary to take into account the nonquenched orbital-angular momentum of the iron ion; this momentum gives rise to magnetic anisotropic interactions between the ions. A complete spectrum then involves transitions from the ground state to the excited states determined by the splitting due to the spin-orbit coupling and the trigonal crystal field, as well as isotropic and perhaps anisotropic exchange effects. Such a calculation has been performed by Grover,[24] Buyers *et al.* on $KCoF_3$,[25] and Chou and Fan on CoO.[9] But new experimental results are undoubtedly needed to justify such a treatment. Further experiments, like Raman light scattering and antiferromagnetic resonance may give useful complementary information on the spin excitation spectrum.

V. CONCLUSION

The dispersion curves of the spin waves in the antiferromagnetic $Fe_{1-x}O$ have been measured at liquid-helium temperature by inelastic neutron scattering. The main difficulty in determining the curves arises from the relative bad quality of the crystal and from its polydomain structure. A Hamiltonian with exchange integrals extended to second metallic neighbors and with single-ion anisotropy (axial-field term) gives satisfactory fitting and leads to reasonable values of the parameters. Physical properties were calculated and compared with other experiments. Further experimental work with neutrons or other techniques, as well as new theoretical calculations, would be useful to explain completely the spin dynamics of $Fe_{1-x}O$.

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