Selective Heating Mechanism of Magnetic Metal Oxides by Alternating Magnetic Field in Microwave Sintering Process

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The mechanism of rapid and selective heating of magnetic metal oxides under the magnetic field of microwaves, which continues beyond the Curie temperature $T_C$, is identified by using the Heisenberg model. Monte Carlo calculations based on the energy principle show that such heating is caused by non-resonant response of electron spins in the unfilled 3d shell to the wave magnetic field. Small spin reorientation thus generated leads to a large internal energy change through the exchange interactions between spins, which becomes maximal around $T_C$ for magnetite $\text{Fe}_3\text{O}_4$. The dissipative spin dynamics simulation yields the imaginary part of the magnetic susceptibility, which becomes largest around $T_C$ and for the microwave frequency around 2 GHz. Hematite $\text{Fe}_2\text{O}_3$ with weak spontaneous magnetization responds much less to microwaves as observed in experiments. The heating of titanium oxide by microwave magnetic field only when oxygen defects are present is also explained by our theory in terms of the absence of spontaneous magnetization.

I. INTRODUCTION

Microwave sintering is the process in which electromagnetic energy of microwaves is delivered directly to electrons or atoms in materials. It enables rapid heating that leads to melting and recrystallization of original solid matters. A laboratory experiment demonstrated that a grained magnetite sample was heated to above 1300°C within a minute by applied microwaves. The amount of energy consumption can be reduced and the release of CO$_2$ gas be halved in the microwave iron making, which reduces energy and environmental problems in modern iron industry. Later it was shown that various metallic oxides including magnetite and titanium oxide with oxygen defects $\text{TiO}_2-x$ ($x > 0$) were sintered quickly at the magnetic field maximum (i.e. the electric field null) in the microwave cavity experiments. The product sintered in the microwave magnetic field was shown to have good magnetic properties as magnets.

The sintering of magnetite/hematite powders of micron sizes is characterized by selective heating. Only the domain of magnetite $\text{Fe}_3\text{O}_4$ with strong magnetization was heated to 1300°C in the microwave magnetic field, which is much above the Curie temperature $T_C$ (585°C). The adjacent domain of hematite $\text{Fe}_2\text{O}_3$ remained at low temperatures. The microwave sintering of magnetic materials is a non-resonant process that occurs with or without a static magnetic field and for any amplitude of wave magnetic field at a fixed microwave frequency. With ferromagnetic metals, microwave resonance absorption and the non-resonant bolometric effect on dc resistance were observed in ferromagnetic resonance (FMR) experiments under microwaves. These phenomena required a static magnetic field of specific strength to have resonance with microwaves, and were observed mainly below room temperature, which are attributed to Joule heating or eddy current. The microwave sintering, which occurs under wide range of strength and frequency of microwave magnetic field without a static magnetic field is physically a different process from the FMR process.

To date, the heating of dielectric materials by the microwave electric field was extensively studied. We examined the heating of water, salt-contained water and ice by microwaves using molecular dynamics simulation. The heating was attributed, respectively, to excitation of electric dipoles, the Joule heating of salt ions, and the weakening of the hydrogen-bonded H$_2$O network by the presence of salt ions. (Pure ice was not heated by 2.5GHz microwave due to tight hydrogen bonds of water molecules.) For bulk metals, microwaves are reflected at the surface due to skin effects and do not transfer energy, while they penetrate into grained metallic powders (10µm in diameter) for a few centimeters and heat them. However, the sintering mechanism of metal oxides that have spontaneous magnetization under the magnetic field of microwaves has not been resolved.

In this paper, we show theoretically that the sintering of particles of magnetic metal oxides, including magnetite and titanium oxide with oxygen defects, by a microwave magnetic field is due to non-resonant response of electron spins in the unfilled 3d shell. We first use the energy principle and perform the Monte Carlo simulations. A small spin perturbation in response to an alternating external magnetic field results in a large internal energy change through exchange interactions. Next, studies in the time domain are done by performing dissipative spin dynamics simulation and detecting the linear response of spins. The temperature and frequency dependence of the heating rate by the microwave magnetic field is obtained on the basis of the imaginary part of magnetic susceptibility $\chi_i$. These results agree well with those by the energy principle, and $\chi_i$ quantitatively accounts for the rapid heating of magnetite in the sintering experiments.
II. NUMERICAL PROCEDURES

We have used the following procedures in our numerical simulations. The magnetization of magnetite and hematite is well described by the Heisenberg model above the Verwey transition temperature (120 K) since electrons are roughly localized. The internal energy $U$ of the magnetic system is represented by the three-dimensional spin vector $s_i$ of the electron at the i-th site, the exchange interaction coefficient $J_{ij}$ between the i-th and j-th sites, and the external magnetic field $B_w$ of microwaves, which reads

$$U(B_w) = - \sum_{i,j} J_{ij} s_i \cdot s_j + \sum_i g \mu_B s_i \cdot B_w. \tag{1}$$

The summation of the exchange interactions in the first term is taken over the pairs of nearest neighbor sites. The magnitude of the spin vector satisfies $|s_i| = S$ for the spin angular momentum $S$. The second term, which may be called the Zeeman term, is the scalar product of magnetization $M = - \sum_i g \mu_B s_i$ and the magnetic field, $- M \cdot B_w$, where $g \approx 2$ and $\mu_B = e h / 2 mc$. We note that the Weiss field (the internal magnetic field) is $B_{W\text{eas}} \approx n_B J_{AB} S / g \mu_B \approx 240$ T, which is much larger than that of microwaves, where $n_B \approx 4.1$ is the effective magneton number of magnetite and $J_{AB}$ is of a few meV. We also note that the individual spin interaction energy $J_{AB} S^2 \approx 0.016$ eV is comparable to the thermal energy at room temperature 0.026 eV. Thus, thermal effects are significant in the sintering process for which temperatures are much above 300 K.

To obtain a thermally equilibrated state, we minimize the internal energy of the spin system Eq.(1) at a given temperature using the Monte Carlo method with the Metropolis criterion. A trial random rotation is exerted on one of the spins in the n-th step: the trial is accepted if the internal energy decreases $\delta U = U^n - U^{n-1} < 0$, or if the energy increase satisfies $\exp(-\delta U / k_B T) > \varepsilon$, where $\varepsilon$ is a random number uniformly generated in the (0,1) interval, $k_B$ is the Boltzmann constant and $T$ is temperature; otherwise the trial is rejected.

To proceed further, we have to specify the crystal structure and the exchange interaction coefficients. For magnetite, the unit cell is a cubic box with the sides of 0.8396 nm at room temperature and contains 24 irons: 16 of them are Fe$^{3+}$ ($3d^6, S = 5/2$) and occupy all the tetrahedral sites (A-site, 8 positions) and half of the octahedral sites (B-site). The rest of irons are 8 Fe$^{2+}$ ($3d^6, S = 2$), and are located at B-sites. The exchange interaction coefficients are all negative and satisfy $|J_{AB}| > |J_{AA}|, |J_{BB}|$. We assume $J_{AB} = -4.0$ meV and $J_{AA} = J_{BB} = -0.3$ meV, where the former is larger in magnitude than the theoretically estimated value 2.5 meV to reproduce $T_c$ in our model.

III. RESULTS

Using the procedures described in Sec.II, we first calculate the equilibrated state without an applied magnetic field for the periodic crystal of magnetite with 3 x 3 x 3 unit cells. Below $T_c$, spins are ordered along the c-axis due to the exchange interactions, with the spins at A-sites and those at B-sites oriented oppositely. The temperature dependence of magnetization calculated with our model is shown in Fig.1. The validity of our model is confirmed by the numerical result that the spontaneous magnetization decreases monotonically with temperature and vanishes above $T_c$, as expected. Our calculated value $M_c / M_0 \approx 1.1$ at 300 K roughly agrees with the experimental value $M_c / M_0 \approx 1.32$, where $M_0 = N \mu_B$ with $N$ the number of irons in the system.

Next, we apply a slowly varying magnetic field $B_w$ to the equilibrium obtained above, and perform the Monte Carlo simulation. The varying speed of the magnetic field is chosen to be slow enough for spins to relax to the state of an instantaneous magnetic field. The amplitude of the magnetic field is 1 T unless otherwise specified, which is still by two orders of magnitude less than the Weiss field. Spins relax in orientation under the magnetic field and the internal energy $U(B_w)$ depends on the magnitude and orientation of $B_w$. We evaluate the difference between the maximum and minimum of the internal energy during a period of the magnetic field change,

$$\Delta U^{(mc)} = U^{(mc)}_{\text{min}} - U^{(mc)}_{\text{max}}. \tag{2}$$

Here, the superscript (mc) stands for "Monte Carlo" simulation. The energy $\Delta U$ that is to be released irreversibly to lattice atoms by dissipation process, possibly
FIG. 2: Model calculation for the magnetic field effects on magnetite at 700 K. The changes in (a) the z-component of magnetization \( M_z = -\sum g\mu_B s_z,i \), (b) the internal energy \( U \) per Fe (solid line), and the contribution of the Zeeman term to the internal energy (dashed line, for which the zero baseline is shifted downward by \( 7U_0 \)) are shown against (c) the applied magnetic field \( B_z \) in the Monte Carlo simulation steps. The z-axis is parallel to the c-axis. The normalization factors are as follows: \( M_0 = N\mu_B \), \( U_0 = 10^{-21} \) J, and \( B_0 = 1 \) T.

by spin-lattice interactions, is obtained by subtracting from \( \Delta U^{(mc)} \) the reversible energy change, \( \Delta U^{(rev)} = U_{max}^{(rev)} - U_{min}^{(rev)} \). The latter is obtained by solving the spin dynamics equation without dissipation,

\[
\dot{s}_i = \sum_j \left( 2J_{ij}/\hbar \right) s_i \times s_j - (g\mu_B/\hbar)s_i \times B_w. \tag{3}
\]

The energy difference \( \Delta U \) can be used as the index of heating by the microwave magnetic field. This is verified later by agreement of the estimation based on the imaginary part of the magnetic susceptibility with the \( \Delta U \) here and also the experimental value of the heating rate.

Figure 2 shows the changes in (a) the average magnetization in the z direction (c-axis), (b) the total internal energy (solid line) and the contribution of the Zeeman term (dashed line) at 700 K against (c) the alternating magnetic field which is parallel to the c-axis. In the present case, the magnetization \( M_z \) stays negative along the z-axis, and the Zeeman term \( -M \cdot B_w \) takes positive or negative value according to whether \( B_w \) is parallel or anti-parallel to the c-axis. In the phase where the applied magnetic field becomes more negative, the magnitude of magnetization increases due to alignment of spins parallel to the c-axis, and the internal energy becomes minimal in this phase of the magnetic field. We note that the large change in the internal energy occurs through the exchange interactions because the energy associated with the Zeeman term is small and reversible, with the former by a factor of \( J_{AB} S/ g\mu_B B_w \) (\( \gg 1 \)) larger than the latter, as depicted in Fig.2(b). In fact, the contribution of the Zeeman term is small and roughly the same as that obtained with the dissipationless spin dynamics Eq.(3).

The distribution functions at the 1.25 \( \times 10^6 \)th Monte Carlo step in Fig.2 are shown in Fig.3. The x and z directions are taken along the a- and c-axes, respectively. In the x direction, the spins form centered Boltzmann distributions and no magnetization occurs along this direction. In the z direction, the spins are aligned parallel to the c-axis. This is consistent with the large negative value of the magnetic field. The distribution functions in the upper panels correspond to \( Fe^{3+} \) (the shaded area denotes the states of spins at A-sites) and those in the lower panels correspond to \( Fe^{2+} \).
FIG. 5: Temperature dependence of the internal energy change (per Fe) $\Delta U$ for hematite is shown by triangles, and that of magnetite with the magnetic field parallel to the c-axis is shown by filled circles as reference, for $B_w = 1$ T ($U_0 = 10^{-21}$ J). The imaginary part of the magnetic susceptibility obtained by dissipative spin dynamics Eq.(4) for $\tau_D = 1$ ns is shown by double circles (in mol$^{-1}$). The vertical line denotes $T_c$ of magnetite. (The shaded areas correspond to the Fe$^{3+}$ at A-sites.) Ferrimagnetization occurs along the z direction. The Fe$^{3+}$ spins at A-sites are anti-parallel to the z-axis and those of Fe$^{2+}$ and Fe$^{3+}$ at B-sites are parallel to it. The change in the orientations in response to the microwave magnetic field is subtle, yet it gives rise to a maximum in the magnitude of magnetization periodically, as shown in Fig.2(a).

Figure 4 shows the calculated temperature dependence of the internal energy difference $\Delta U = \Delta U^{(\text{mc})} - \Delta U^{(\text{rev})}$ when the microwave magnetic field is parallel either to the c-axis (filled circles) or to the a-axis of magnetite (open circles). The difference in the energy becomes largest when the polarization of the magnetic field is parallel to the c-axis, and it increases linearly with temperature up to $T_c$. The change in the reversible energy $\Delta U^{(\text{rev})}$ and that in the Zeeman term for the former case are shown by crosses and filled squares, respectively. The energy change $\Delta U^{(\text{rev})}$ is similar to that in the spontaneous magnetization which decreases with temperature and vanishes above $T_c$. The change in the Zeeman term is almost the same as $\Delta U^{(\text{rev})}$ but is finite for $T > T_c$. The Zeeman term in the Monte Carlo simulation remains finite because an induced magnetization appears synchronously with and along the magnetic field independently of its polarization in the paramagnetic regime. The major contribution to the internal energy difference $\Delta U$ is attributed to the exchange interactions since the change in the Zeeman term is reversible and thus almost subtracted in $\Delta U$. The temperature dependences shown in Fig.4 are in excellent agreement with the sintering experiments in the microwave magnetic field$^{3,4}$, where the heating of magnetite was enhanced at 300 – 600$^{\circ}$C and continued to much above $T_c$.

An argument that involves time scales as well as the temperature dependence of heating is made possible by solving the dissipative spin dynamics. Here, the term $-(s_i - s_{i0})/\tau_D$ is added to the righthand side of Eq.(3). Namely, we solve

$$\frac{ds_i}{dt} = \sum_j \frac{(2J_{ij}/\hbar)s_i \times s_j - (g\mu_B/\hbar)s_i \times B_w}{\tau_D} - (s_i - s_{i0})/\tau_D. \quad (4)$$

A set of $s_{i0}$ constitutes the equilibrium spin distribution function for a given temperature and magnetic field under the Monte Carlo calculation. The imaginary part of the magnetic susceptibility $\chi_\imath$ is obtained from the linear response of magnetization against the applied alternating magnetic field. $\chi_\imath$ gives the heating rate $dT/dt \propto \chi_\imath$, and is shown for magnetite with double circles in Fig.5. It peaks around 800 K and is consistent with $\Delta U$ obtained with the energy principle of the Monte Carlo calculation.
The dependence of the imaginary part of magnetic susceptibility $\chi_i$ on the relaxation time $\tau_D$ is shown in Fig. 6 for the 2.5 GHz microwave. We see that $\chi_i$ is inversely proportional to $\tau_D$ in the $\tau = 2\pi/\omega \leq \tau_D$ range. Also, the dependence of $\chi_i$ on the microwave frequency is shown in Fig. 7 for $\tau_D = 1$ ns. The imaginary part of magnetic susceptibility peaks around 2 GHz. This agrees with the experimentally deduced magnetic permeability for magnetite. In our calculation, the relaxation time is assumed to be constant irrespectively of temperature or microwave frequency. However, if the relaxation time becomes small with temperature rise, the heating rate increases as $\tau_D^{-1}$ as shown in Fig. 5, resulting in more rapid heating at elevated temperatures.

From these data, one obtains the heating rate $dT/dt \sim (1/2)\omega^2B_{mw}^2c_p/\chi_i \approx 300$ K/s for the case of $\tau_D = 1$ ns and the microwave field $B_{mw} = 150$ G, where the heat capacity $c_p$ is 210 J/K mol at 600K (the wave period is 400 ps for the 2.45GHz microwave). This is large enough to account for the experimental value $(dT/dt)_{ex} \approx 250$ K/s in the microwave sintering of magnetite.

The dependence of the internal energy change in magnetite per wave period on the applied magnetic field is shown in Fig. 8. The magnetic field amplitude ranges from 0.125 T to 1.0 T. It is well fitted by the quadratic law $B^2$, therefore, $\Delta U$ thus the heating rate is proportional to the microwave power.

Hematite has a different crystal structure from magnetite and has weak spontaneous magnetization. The calculated change in the internal energy $\Delta U$ is plotted for various temperatures by triangles in Fig. 5. By comparison of $\Delta U$ with the case of magnetite, the response of hematite to the alternating magnetic field is considerably weak. This is consistent with the experimental fact that only the domain of magnetite in a magnetite-hematite composite powder was heated by the magnetic field of microwaves.

The observation that heating of titanium oxide occurs only when oxygen defects are present, $\text{TiO}_2-x$ ($x > 0$), is explained in a similar fashion. Titanium in titanium oxide $\text{TiO}_2$ is a $\text{Ti}^{3+}$ ion with $3d^0$ electron configuration, which has no electrons in the 3d shell. Thus, it has no spontaneous magnetization and should not respond to microwave magnetic field, similarly with hematite. However, when there are oxygen defects, the trivalent titanium ions $\text{Ti}^{3+}$ appear which have $3d^1$ electron configuration. The spins of these 3d electrons respond to the magnetic field of microwaves, and absorb microwave energy which leads to observed heating under the microwave magnetic field.

IV. SUMMARY

In this paper, we have showed theoretically the mechanism of the rapid and selective sintering of magnetic metal oxide particles by the magnetic field of microwaves. We adopt the Heisenberg model, and perform both Monte Carlo calculation and dissipative spin dynamics simulations. The heating occurs due to the response of magnetization to microwaves, which originates from electron spins residing in the unfilled 3d shell. Their non-resonant response causes a large change in the internal energy through the exchange interaction between spins. It persists above the Curie temperature $T_c$ because each electron spin is able to respond to the alternating magnetic field of microwaves even above $T_c$. This energy change will then be dissipated to lattices and contribute to heating.

Hematite $\text{Fe}_2\text{O}_3$ which has only weak spontaneous magnetization shows much less response to microwaves than magnetite. Also, the heating of titanium oxide having oxygen defects $\text{TiO}_2-x$ $(\chi_i 0)$ by the microwave magnetic field is explained by our theory in terms of intrinsic (spontaneous) magnetization.

The imaginary part of the magnetic susceptibility $\text{Im} \chi$ obtained by solving dissipative spin dynamics agrees well with the heating results by the Monte Carlo calculation. We have also presented the dependences of the heating rate on the frequency of microwaves and on the spin relaxation time. These results well account for the large heating rate of magnetic metal oxide by the microwave magnetic field in the sintering experiments.

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