Relaxation dynamics of iron-group dihalides

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(Received 3 August 2005; revised manuscript received 12 September 2006; published 6 February 2007)

In this study, the relaxation dynamics of iron-group dihalides by making use of spin-1/2 metamagnetic Ising model has been formulated by the method of thermodynamics of irreversible processes. Using a molecular field approximation for the magnetic Gibbs energy, the magnetic Gibbs energy production in the irreversible process is calculated and time derivatives of the order parameters are treated as fluxes conjugate to their appropriate generalized forces in the sense of Onsager's theory of irreversible thermodynamics. Two relaxation times are calculated and their temperature variances are examined. Moreover, the phase transition behaviors of the relaxation times are also obtained anaytically via the critical exponents.

DOI: 10.1103/PhysRevE.75.021104 PACS number(s): 05.50.+q, 05.70.Ln, 64.60.Cn, 64.60.Ht

I. INTRODUCTION

The unusual magnetic properties of the iron-group (anhydrous) dihalides have made these compounds a subject of considerable experimental and theoretical interest for many years [1,2]. These materials are grouped as metamagnetic substances since their unorthodox magnetic properties do not allow them to be classified either as ferromagnets or as antiferromagnets. Ising metamagnets, systems which exhibit ferromagnetic and antiferromagnetic couplings simultaneously can induce novel kinds of critical behavior by forcing competition between these couplings, in particular when a field is applied. The transition in these materials are field induced transitions which is distinguished from other magnetization processes. $FeCl_2$ and $FeBr_2$ are well-known Ising type metamagnets [3,4]. In these structures, in the antiferromagnetic phase when the iron ions in the triangular layers order ferromagnetically, a layer with a negative sign follows a layer with a positive sign. Due to this fact, the external field acts differently on the oppositely oriented layers which leads to different ordered states and associates a sequence of phase transitions as a function of these two interaction strengths. Such models were originally formulated in order to give help in describing the complex magnetism of rare earths [5].

The dynamics of the metamagnetic systems were investigated by Monte Carlo simulations with Kawasaki dynamics [6,7], three-spin flip dynamics [8], dynamic Monte Carlo renormalization group method [9], and Glauber dynamics [10]. Onsager's reciprocity theorem [11] deduced by the application of time reversal symmetry to microscopic fluctuations can be used in investigating the coupled irreversible processes, such as relaxation of order parameters in spin systems. According to Onsager's irreversible thermodynamics, the thermodynamic forces and fluxes are linearly related. This method has been successfully applied to many irreversible processes near equilibrium, such as transport in homogenous media [12], the gyrothermal effect with polyatomic gases [13], steady state interface motion during phase transformation in a two component system [14], and mass and energy flow across the interface between dilute and condensed phases [15].

The aim of this study is to formulate the dynamics of the Ising metamagnetic system and to study the field and temperature dependence of the relaxation times via the phenomenological kinetic coefficients. In particular we investigate the behaviors of these relaxation times near the phase transition temperatures. In order to establish this we used a method where the equilibrium statistical theory and thermodynamics of irreversible processes are combined. This type of calculation was first performed for an *AB* type alloy by Tanaka *et al.* [16], and an *AB* type ferromagnetic and antiferromagnetic Ising model by Barry [17] and Barry and Harrington [21]. Recently Erdem and Keskin and co-workers investigated the dynamical behavior of the spin-1 Ising model extensively with this method [18,19].

The layout of the paper is as follows: in Sec. II we give a brief description of the model. In Sec. III we obtain the free energy production for the Ising metamagnet in an axial magnetic field within the framework of molecular field theory. Then in Sec. IV, relaxation behavior of the system near the critical and multicritical points is analyzed. Finally, a summary and discussion of the results are given in the last section.

II. EQUILIBRIUM PROPERTIES OF THE ISING METAMAGNETIC MODEL WITHIN THE FRAMEWORK OF MOLECULAR FIELD THEORY

The system under consideration is the spin-$\frac{1}{2}$ Ising metamagnet described by the Hamiltonian

$$\hat{H} = -\sum_{nn} J_1 s_j s_k - \sum_{nnn} J_2 s_j s_k - \sum_j H s_j, \qquad (1)$$

where $s_j = \pm 1$ is an Ising spin, the first term denotes the exchange interaction with the nearest neighbor spin in the

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neighbor layers whereas the second term gives the exchange interaction of the considered spin with the neighboring spins in its layer. H is the magnitude of the external field acting on the system. As mentioned above, interlayer orientation is ferromagnetic ($J_2>0$) whereas the intralayer interaction is antiferromagnetic ($J_1<0$). Following previous considerations [4], the basic equations of the mean field theory can be obtained as

$$x = \tanh\{\beta(H + z_2 J_2 x + z_1 J_1 y)\},$$

$$y = \tanh\{\beta(H + z_1 J_1 x + z_2 J_2 y)\}, \quad (2)$$

where x and y are sublattice magnetizations;

$$x = \langle s_i \rangle_A \quad y = \langle s_j \rangle_B, \quad (3)$$

where $\langle \ldots \rangle$ is the thermal expectation value. These equations may be solved without difficulty by an iterative procedure. The solutions correspond to the extremum of the free energy so that one has to determine the solution that minimizes $\boldsymbol{G}$ [4]. The system under investigation is a system which is constituted from the metamagnetic Ising spins on the simple cubic lattice. Thus the coordination number for ferromagnetic interaction is 4 ($z_2=4$) whereas the coordination number for antiferromagnetic interaction is 2 ($z_1=2$). It is known that the Ising metamagnet exhibits two kinds of phase diagrams in the (T,H) plane depending on the ratio $\eta=\frac{z_2 J_2}{z_1|J_1|}$ [4,22]. In both cases, the transitions between the antiferromagnetic and paramagnetic phases are of first order at low temperatures and strong fields while it is of second order at higher temperatures. In the case of simple cubic lattice if $\eta > 0.6$, the two types of transitions are connected by a tricritical point [22], see Fig. 1(a). At weak fields H and low temperatures T, the spins order antiferromagnetically with the magnetization per layer changing sign from one layer to the adjacent one. The spins tend to orient in the direction of the field. If the field has a positive value then it will tend to increase the number of "+" spins. The ferromagnetic structure is stable at zero temperature for fields exceeding the critical field value $H_c=z_1|J_1|$ [23]. On the other hand if $0 < \eta < 0.6$, the tricritical point decomposes into a critical end point (CEP) and a double critical end point (BCP) with a line of first order transitions in between, separating two antiferromagnetic phases [22], see Figs. 1(b) and 1(c). Consequently in the molecular field theory (MFT) it is only the ratio η which really determines the phase diagram.

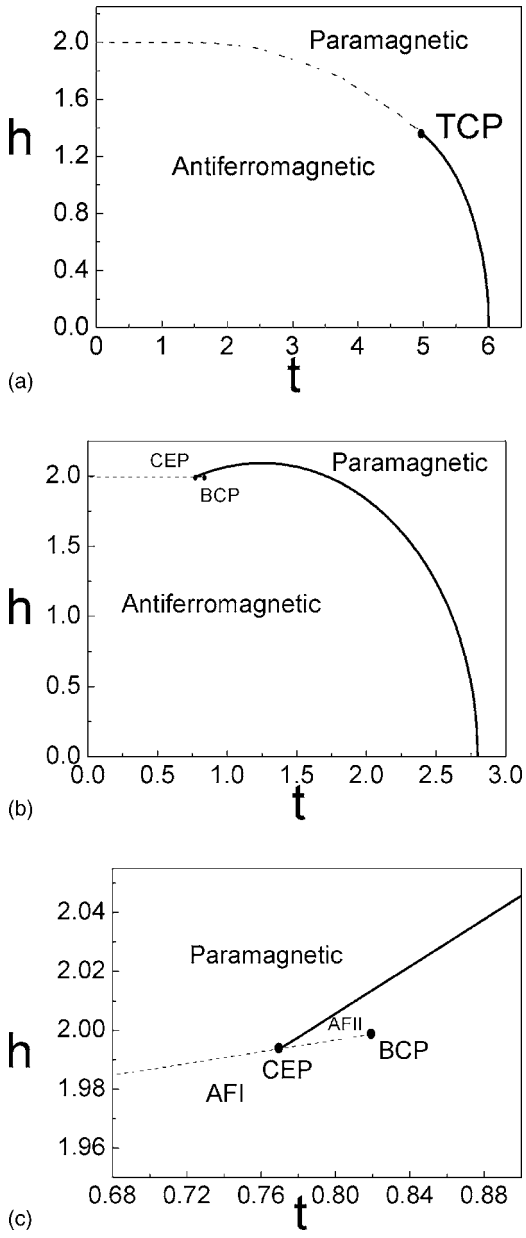

FIG. 1. (a) Mean field phase diagram of the Ising metamagnet in the (h,t) plane, where t, h are reduced temperature, and field, respectively ($t=\frac{k_B T}{|J_1|}$, $h=\frac{H}{|J_1|}$) for $\eta=\frac{z_2 J_2}{z_1|J_1|}=2.0$, TCP denotes the tricritical point (b) the same as (a) but for $\eta=0.4$; CEP, BCP denotes critical end point and double critical end point, respectively. (c) An enlargement near the CEP. The dotted lines denote the coexistence curve and solid lines denote the λ line.

III. FREE ENERGY PRODUCTION FOR THE ISING METAMAGNET IN AN AXIAL MAGNETIC FIELD

Let us at first introduce two new variables; the normalized total magnetization m and the normalized staggered magnetizaton s,

$$2m = x + y,$$

$$2s = x - y. \quad (4)$$

In general for metamagnetic systems we should say that a phase is antiferromagnetically ordered if $0<|s|\leqslant 1$ and paramagnetic if the two sublattice magnetization are equal ($s=0$, although m may be nonzero if a magnetic field is present). The free energy expression given in Ref. [4] could be written in terms of staggered and total magnetization by making use of Eq. (4) as follows:

$$\boldsymbol{G}(m,s,T,H) = \Big\{-\tfrac{1}{2}z_1 J_1(m^2 - s^2) - \tfrac{1}{2}z_2 J_2(m^2 + s^2) - NHg\mu_B m + \tfrac{kT}{4}\{(1+m+s)\ln(1+m+s) + (1-m-s)\ln(1-m-s) + (1+m-s)\ln(1$$

$$+ m - s) + (1 - m + s)\ln(1 - m + s)\}, \tag{5}$$

where N, k_B, g, μ_B are the total number of Ising spins, Boltzmann's constant, spin factor, and the Bohr magneton, respectively, whereas z_2 and z_1 denote the coordination numbers in the same neighboring layer. In order to investigate relaxation phenomena in this system, we assume that the value of the applied field is departed slightly from its equilibrium value. This removes the spin system slightly from its equilibrium state, and we can study how rapidly the spin system returns or relaxes back to thermal equilibrium. For the model considered here, with $J_1 \neq 0$ phase transition lines occur at places which are away from the $H \neq 0$ axis [23]. Thus the magnetic Gibbs energy given by Eq. (5) is written in the neighborhood of equilibrium as $\boldsymbol{G}(m,s,T,H) = \boldsymbol{G}^{(0)} \times (m_0, s_0, T, H_0) + \Delta \boldsymbol{G}$, where $\boldsymbol{G}^{(0)}$ is the equilibrium magnetic Gibbs energy for the case $m = m_0$, $s = s_0$, $H = H_0$ and ΔG is the production of the magnetic Gibbs energy due to the variance of the external field $(H - H_0 \neq 0)$, and is given in the following form:

$$\begin{aligned}\Delta \boldsymbol{G} = \frac{1}{2}\{&A(m-m_0)^2 - 2B(s-s_0)(m-m_0) + C(m-m_0)^2 \\ &- 2D(H-H_0)(m-m_0) - 2E(H-H_0)(s-s_0) \\ &+ F(H-H_0)^2 + 2G((H-H_0)\ \}, \end{aligned} \tag{6}$$

where

$$A = \left(\frac{\partial^2 \boldsymbol{G}}{\partial m^2}\right)_{eq},$$

$$= -N\left\{z_1 J_1 + z_2 J_2 - \frac{kT}{4}\left(\frac{1}{1+m_0+s_0} + \frac{1}{1-m_0-s_0} + \frac{1}{1+m_0-s_0} + \frac{1}{1-m_0+s_0}\right)\right\},$$

$$B = -\left(\frac{\partial^2 \boldsymbol{G}}{\partial s \partial m}\right)_{eq},$$

$$= -\frac{NkT}{4}\left\{\left(\frac{1}{1+m_0+s_0} + \frac{1}{1-m_0-s_0} - \frac{1}{1+m_0-s_0} - \frac{1}{1-m_0+s_0}\right)\right\},$$

$$C = \left(\frac{\partial^2 \boldsymbol{G}}{\partial s^2}\right)_{eq},$$

$$= N\left\{z_1 J_1 - z_2 J_2 + \frac{kT}{4}\left(\frac{1}{1+m_0+s_0} + \frac{1}{1-m_0-s_0} + \frac{1}{1+m_0-s_0} + \frac{1}{1-m_0+s_0}\right)\right\},$$

$$D = -\left(\frac{\partial^2 \boldsymbol{G}}{\partial H \partial m}\right)_{eq} = Ng\mu_B,$$

$$E = -\left(\frac{\partial^2 \boldsymbol{G}}{\partial H \partial s}\right)_{eq} = 0,$$

$$F = \left(\frac{\partial^2 \boldsymbol{G}}{\partial H^2}\right)_{eq} = 0,$$

$$G = \left(\frac{\partial \boldsymbol{G}}{\partial H}\right)_{eq} = -Ng\mu_B m_0, \tag{7}$$

where all the derivatives are evaluated for $m = m_0$, $s = s_0$, $H = H_0$.

IV. DERIVATION OF KINETIC EQUATIONS AND THE RELAXATION TIMES

According to the theory of irreversible thermodynamics, one obtains the generalized forces X_m, X_s conjugate to the currents $\dot{m}, \dot{s}$ respectively, by differentiating $\Delta \boldsymbol{G}$ with respect to $(m - m_0)$, $(s - s_0)$, and $(H - H_0)$,

$$X_m = \frac{\partial \Delta G}{\partial (m - m_0)} = A(m - m_0) - B(s - s_0) - D(H - H_0),$$

$$X_s = \frac{\partial \Delta G}{\partial (s - s_0)} = C(s - s_0) - B(m - m_0). \tag{8}$$

Again, according to Onsager's theory of irreversible thermodynamics, the linear relations between the currents and forces may be written in terms of a matrix of phenomenological rate coefficients where off diagonal elements are equal to each other (the matrix is symmetric since both m and s are odd variables under time inversion [24]):

$$\begin{bmatrix} \dot{m} \\ \dot{s} \end{bmatrix} = \begin{bmatrix} \gamma_m & \gamma \\ \gamma & \gamma_S \end{bmatrix} \begin{bmatrix} X_m \\ X_s \end{bmatrix}. \tag{9}$$

Consequently, this matrix equation can be written in component form using Eqs. (8), namely a set of two coupled, linear inhomogenous first order rate equations. In order to obtain the relaxation times, one considers the corresponding homogenous equations resulting when the external field is equal to its equilibrium value, i.e., $H = H_0$. Then Eq. (9) becomes

$$\begin{bmatrix} \dot{m} \\ \dot{s} \end{bmatrix} = \begin{bmatrix} \gamma_m A - \gamma B & \gamma C - \gamma_m B \\ \gamma A - \gamma_s B & \gamma_s C - \gamma B \end{bmatrix} \begin{bmatrix} m - m_0 \\ s - s_0 \end{bmatrix}. \tag{10}$$

Assuming a solution of the form $e^{-t'/\tau}$ for Eq. (10) and since one can show that $|B^2 - AC| \ll 1$ in the neighborhood of the critical temperature $T_c(H)$, the resulting relaxation times can be found from the secular equation and may approximately be given as

$$\frac{1}{\tau_1} = -\gamma_m C\left(1 + \frac{\gamma_s A}{\gamma_m C}\right) - \frac{1}{\tau_2},$$

$$\frac{1}{\tau_2} = \frac{\gamma_m \gamma_s - \gamma^2}{\gamma_s} \frac{B^2/C - A}{1 + \gamma_m A/\gamma_s C}. \tag{11}$$

One observes that the off-diagonal rate coefficient γ which couples the total and staggered magnetization currents in Eq. (9) appears in Eq. (11) solely through the factor $(\gamma_m\gamma_s-\gamma^2)$. The assumption made in this paper is that γ^2 is negligible compared to $\gamma_m\gamma_s$ for temperatures close to $T_c(H)$, i.e.,

$$\gamma_m\gamma_s - \gamma^2 \approx \gamma_m\gamma_s \tag{12}$$

for the temperatures T near $T_c(H)$. Strictly speaking, assumption (12) may be verified only by a theory external to irreversible thermodynamics [17]. In this regard, Kikuchi has shown that [25], using a more powerful statistical mechanical method called path probability, the assumption (12) is valid for order-disorder configuration relaxation in a bcc AB-type lattice and for relaxation in a one-dimensional Ising model of ferromagnetism. In fact, it is shown by Kikuchi that the latter problem exhibits $\gamma=0$ for $T<T_c$. A similar result for the present problem would imply from Eq. (9) that the total magnetization m and the staggered magnetization s relax independently from one another at temperatures above T_c with relaxation times essentially τ_1 and τ_2, respectively. One may not, however, conclude such exact results from the method or the assumption [12] used in this paper. The staggered and total magnetization m and s approach to their equilibrium values m_0 and s_0 with two reduced characteristic times τ_1 and τ_2 given by Eq. (11).

The behavior of these relaxation times near the phase transition points can be obtained analytically from the critical exponents. Let

$$\delta T = T_c - T,$$

$$\delta H = H_c - H \tag{13}$$

represent the measure of the deviations of temperature and field from the critical values. On the other hand, near the critical point, taking δT and δH as expansion parameters, the relaxation times can be written in the form

$$\tau_1 = \frac{\gamma_s C + \gamma_m A}{\gamma_m\gamma_s(B^2 - AC)},$$

$$\tau_2 = \frac{1}{(\gamma_s C + \gamma_m A)[1 + \gamma_m\gamma_s(B^2 - AC)/(\gamma_s C + \gamma_m A)^2]}, \tag{14}$$

where A, B, C becomes

$$A = -N\left\{z_1J_1 + z_2J_2 - \frac{k(T_c-\delta T)}{4}\left(\frac{1}{1+m_0+s_0} + \frac{1}{1-m_0-s_0} + \frac{1}{1+m_0-s_0} + \frac{1}{1-m_0+s_0}\right)\right\},$$

$$B = -\frac{NkT}{4}\left\{\left(\frac{1}{1+m_0+s_0} + \frac{1}{1-m_0-s_0} - \frac{1}{1+m_0-s_0} - \frac{1}{1-m_0+s_0}\right)\right\},$$

$$C = N\left\{z_1J_1 - z_2J_2 + \frac{k(T_c-\delta T)}{4}\left(\frac{1}{1+m_0+s_0} + \frac{1}{1-m_0-s_0} + \frac{1}{1+m_0-s_0} + \frac{1}{1-m_0+s_0}\right)\right\}. \tag{15}$$

As it is stated in Sec. III for $H\neq 0$, m will have a value different from zero at the phase transition point. On the other hand, staggered magnetization can be expressed in the vicinity of T_c and for the critical value of the field ($\delta H=0$) as

$$s_0(\delta T,0) \sim (\delta T)^{1/2} \tag{16}$$

for $\eta>0$ where the system undergoes a second-order phase transition, and here the $\sim$ sign is well advised as it is important to remember that $s_0(\delta T,0)$ only represents the asymptotic behavior of the function $s_0(\delta T,0)$ as $\delta T\to 0$. More generally one might expect $s(\delta T,0)=A|T|\lambda(1+b\delta T^{\lambda_1}+\cdots)$, where $\lambda_1>0$. At low temperatures the system undergoes a first order phase transition and at the vicinity of this transition the staggered magnetization vanishes at T_c as

$$s_0(\delta T,0) \sim (-\delta T)^{1/2} \tag{17}$$

for $\eta>0$, only if for $\eta>0.6$ the critical point of the phase separation lies on the Néel line so that the phase diagram exhibits a tricritical point. Just at this point staggered magnetization is

$$s_0(\delta T,0) \sim (-\delta T)^{1/4}. \tag{18}$$

On the other hand, in the case of $0<\eta<0.6$, the phase diagram is rather different. The tricritical point decomposes into a CEP and a BCP. At both points the staggered magnetization scales as [4,26],

$$s_0(\delta T,0) \sim (\delta T)^{1/2}. \tag{19}$$

Finally for high temperatures and low field values the system undergoes second order phase transitions at which staggered magnetization is $s_0(\delta T,0)\sim(\delta T)^{1/2}$.

The critical exponents for the functions $\tau_1(\delta T,\delta H)$ and $\tau_2(\delta T,\delta H)$ are defined, respectively, as

$$\lambda_1 = \lim_{\delta T\to 0}\frac{\ln|\tau_1(\delta T,0)|}{\ln|\delta T|},$$

$$\lambda_2 = \lim_{\delta T\to 0}\frac{\ln|\tau_1(\delta T,0)|}{\ln|\delta T|}. \tag{20}$$

This definition is valid for all values of $\lambda_i(i=1,2)$ where the negative values correspond to the divergence of the relaxation times $\tau_1(\delta T,\delta H)$ and $\tau_2(\delta T,\delta H)$ as δT goes to zero, the positive values correspond to logarithmic divergence, cusps or jump singularities [27]. On the other hand, in order to distinguish a cusp from a logarithmic divergence another sort of critical exponent, λ_i', is introduced. To find the exponent λ_i' that describes singular parts of τ_1 and τ_2 with a cusplike singularity, we first find the smallest integer k such that the derivatives $\partial^k\tau_1/\partial(\delta T)^k=\tau_1^{(k)}$ and $\partial^k\tau_2/\partial(\delta T)^k=\tau_2^{(k)}$ diverge as $\delta T\to 0$ [27]. We then define

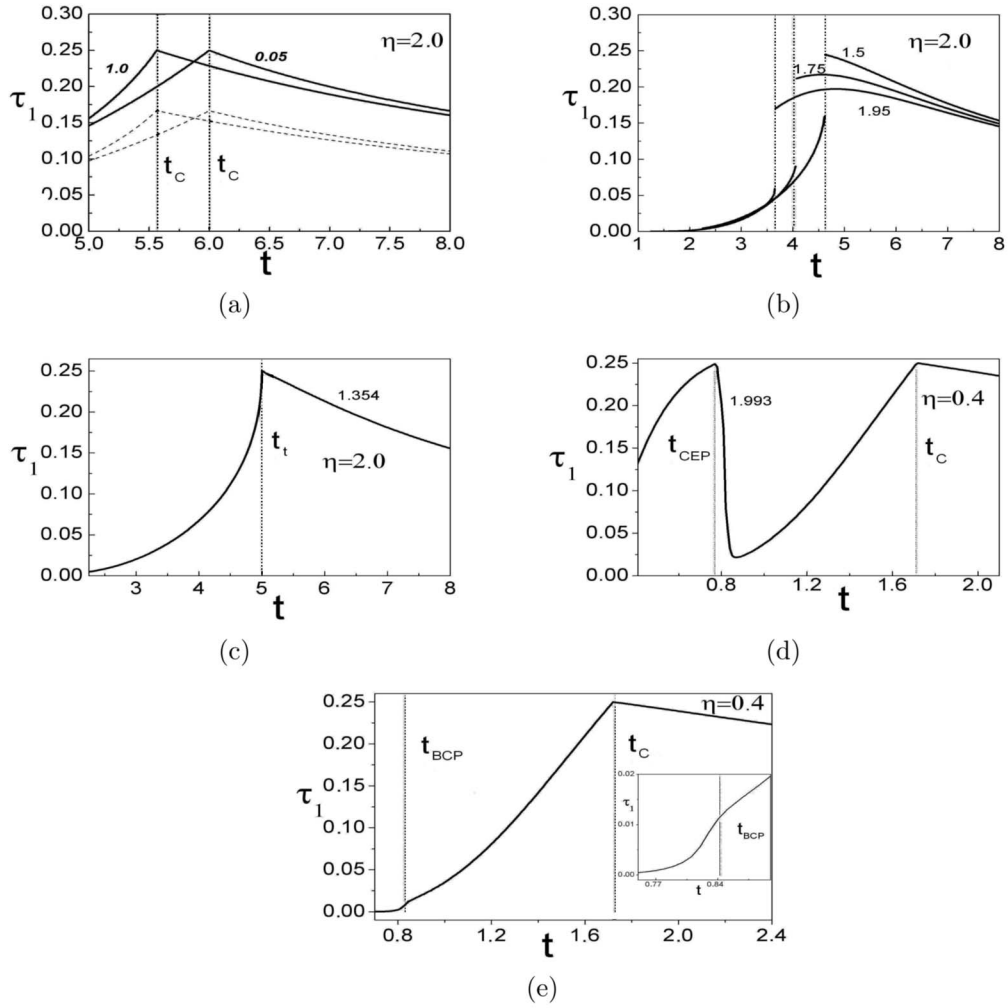

FIG. 2. Relaxation time τ_1 vs reduced temperature $\left(t=\frac{k_BT}{|J_1|}\right)$ for two cases; $\eta=\frac{z_2J_2}{z_1|J_1|}=2.0$ and $\eta=\frac{z_2J_2}{z_1|J_1|}=0.4$. The number accompanying each curve denotes the reduced value of the external field, $h=\frac{H}{|J_1|}$. The vertical dotted lines represent the phase transition temperatures. The solid and dashed curves correspond to $\gamma_m=1$, $\gamma_s=0.1$, $\gamma=10^{-5}$, and $\gamma_m=1.5$, $\gamma_s=0.15$, $\gamma=10^{-5}$, respectively. (a) The system undergoes a second order phase transition; (b) at the first order phase transition point; (c) the system at the tricritical point; (d) at the critical end point and at the second order phase transition point for $h=h_{CEP}$; (e) the system at the bicritical end point and at the second order phase transition temperature for $h=h_{BCP}$.

$$\lambda_i' = k + \lim_{\delta T\to 0} \frac{\ln|\tau_i(\delta T,0)|}{\ln|\delta T|}. \tag{21}$$

The behavior of the relaxation time τ_1 is a function of the reduced temperature, where $t=k_BT/|J_1|$ is shown in Figs. 2(a)–2(e) for several values of reduced field, $h=\frac{H}{|J_1|}$. Figures 2(a)–2(c) correspond to the second order phase transition temperature, first order phase transition temperature, and tricritical point, respectively, for $\eta=2$, whereas in Figs. 2(d) and 2(e) the temperature behavior of the same relaxation time (τ_1) for values of the field which correspond to the critical end point and bicritical end point for $\eta=0.4$ are presented. In the figures, the solid curves are for $\gamma_m=1$, $\gamma_s=0.1$, $\gamma=10^{-5}$, the dashed curves for $\gamma_m=1.5$, $\gamma_s=0.15$, $\gamma=10^{-5}$, and the numbers associated with each curve are the various values of the external field. The vertical dotted lines refer to the phase transition temperatures for each value of the external field. τ_1 scarcely varies with temperature, and slightly increases just below and above the phase transition temperatures. It should be stressed that cusps occurred for τ_1 at the critical, tricritical point, critical end point, and bicritical end point and also at the second order phase transition points which exist on the higher temperature region for $h=h_{CEP}$ and $h=h_{BCP}$ as seen in Fig. 2(a) and Figs. 2(c)–2(e), respectively, since the first derivative of τ_1 for the critical, tricritical points, as well as for the critical end point and bicritical end point diverge as $(\delta T)^{-1/2}$ and $(\delta T)^{-1/4}$, $(\delta T)^{-1/2}$, $(\delta T)^{-1/2}$, respectively when $\delta T\to 0$. Hence from Eq. (21) it follows that $\lambda_1'=1-1/2=1/2$ for second order phase transition temperatures, critical end point and bicritical end point whereas $\lambda_1'=1-3/4=1/4$ for the tricritical case. On the other hand τ_1 displays different behavior at the first order phase transition temperatures. It has a jump discontinuity at the first order phase transition temperatures [see Fig. 2(b)] with $\lambda_1=0$. It should be emphasized that for $h=1.95$ and 1.75 which are fairly close to the critical field value $h_c=z_1=2$ the

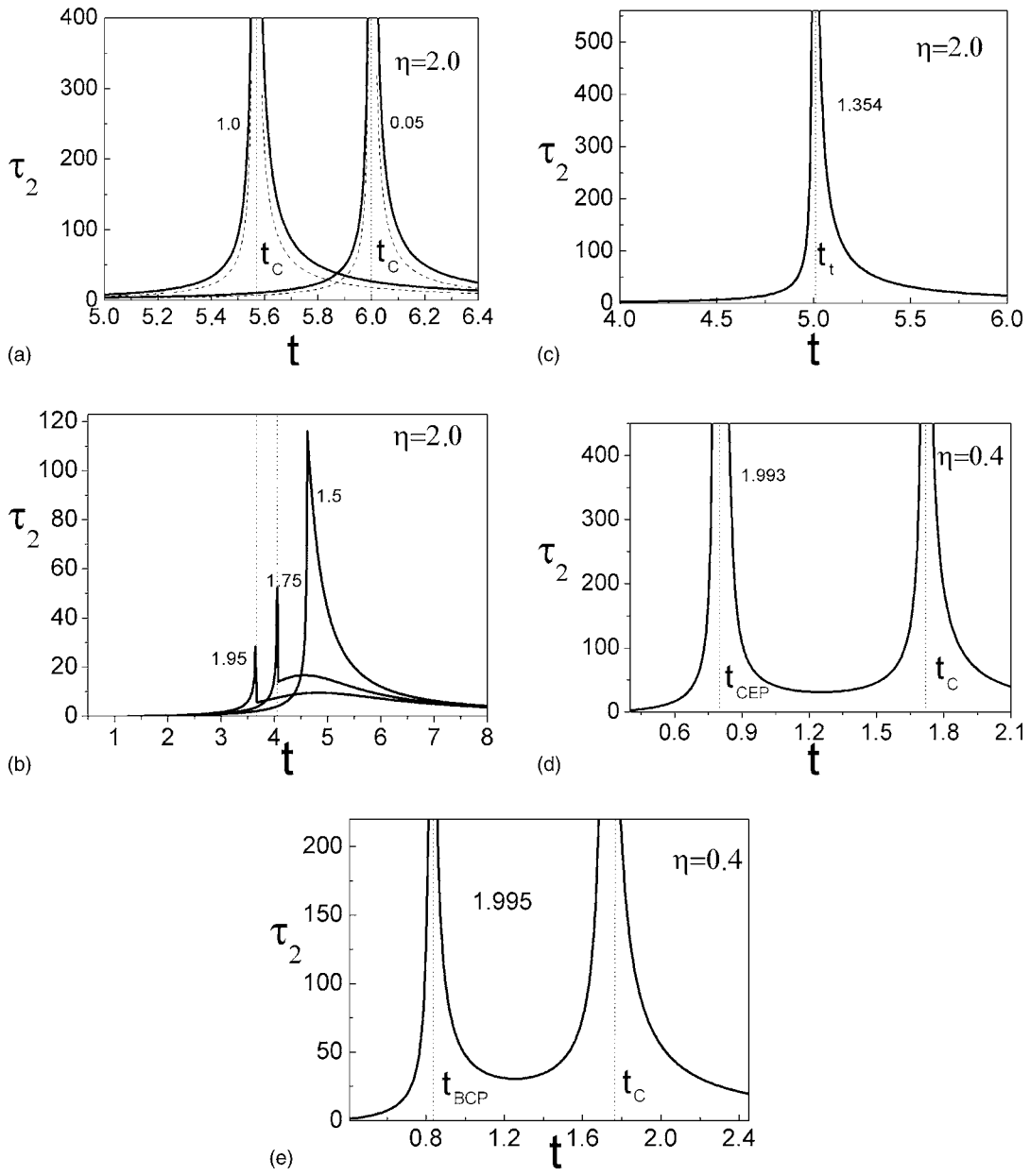

FIG. 3. Same as Fig. 2 but for the relaxation time τ_2.

relaxation time τ_1 has an anomalous peak at higher temperatures. Meanwhile, for $h=1.5$ which is lower relative to them, the relaxation time still shows a jump discontinuity at the transition temperatures, but now there is no anomalous peak. In addition we have found that increasing values of γ_s and γ_m lead to speeding up of the whole relaxation process which can be seen by comparing the dashed and solid curves in Fig. 2(a).

The functional dependence of the relaxation time τ_2 on the temperature is given in Figs. 3(a)–3(e) for several values of the external field, $h=\frac{H}{|J_1|}$, corresponding to the second-order phase transition temperature, first-order phase transition temperature and tricritical point, critical end point and bicritical end point and the second order phase transition points which exist on the higher temperature region, respectively. In these figures, the solid and dashed curves correspond to $\gamma_m=1$, $\gamma_s=0.1$, $\gamma=10^{-5}$, and $\gamma_m=1.5$, $\gamma_s=0.15$, $\gamma=10^{-5}$, respectively, and the numbers on the curves are the values of the reduced external field. The vertical dotted lines illustrate the phase transition temperatures for each value of the external field. In this case, τ_2 increases rapidly with increasing temperature and diverges as the temperature approaches to the second order phase transition point on either side, as seen in Fig. 3(a), since the critical exponents of τ_2 are found to be $\lambda_2=-0.5$ for all coefficients. On the other hand, τ_2 also increases rapidly when the temperature is raised but makes a sharp cusp at the first order phase transition temperature, which is illustrated in Fig. 3(b). It should be remarked that for $h=1.95$ and 1.75, which are rather close to the critical field value $h_c=z_1=2$ the relaxation time τ_2, makes a sharp cusp at the transition temperatures with an exponent $\lambda_2'=1-1/2=1/2$ and have an anomalous peak at higher tem-

peratures. Besides, for $h=1.5$, which is lower relative to the relaxation time τ_1, again shows a sharp cusp at the transition temperatures, but now there is no anomalous peak. The behavior of τ_2 near the tricritical point is plotted in Fig. 3(c). One can see from the figure that τ_2 increases rapidly with increasing temperature and diverges at the tricritical point as in the second order case but with a different critical exponent $\lambda_2=-0.25$. On the other hand, in Figs. 3(d) and 3(e) variation of τ_2 with temperature of the reduced external field values corresponding to critical end point and bicritical end point has been given for $\eta=0.4$. The important feature of the system for $h=h_{CEP}$ and $h=h_{BCP}$ is the existence of second order phase transitions at higher temperature values. This situation could easily be seen in the h-t phase diagram given in Fig. 1(b). As an example, while for $h=h_{CEP}$ CEP takes place in the low temperature region in the antiferromagnetic phase, there is a second order phase transition taking place in the high temperature regime. Similarly, for $h=h_{BCP}$ first-order line segment terminates inside the antiferromagnetic phase at BCP. In addition, there exists a second order phase transition at a higher temperature. In these multicritical points τ_2 diverges with the exponent $\lambda_2=-0.5$. On the other hand, the spin-1 Ising system is investigated for critical end point in Ref. [20]. Also, in agreement with the results of the present work, in Ref. [20], it is seen that in the vicinity of CEP one of the relaxation times exhibits a divergence, while the other makes a cusp. It is worthwhile to mention that the relaxation times near the critical end point as well as their critical behavior via exponents are not obtained in Ref. [20].

We have also found that increasing values of γ_s and γ_m lead to speeding up of the whole relaxation process [compare also the dashed and solid curves in Fig. 3(a)]. At this point, it is convenient to note similar behaviors, such as divergence of one of the relaxation times near the critical point and the finiteness of the other relaxation time are obtained for antiferromagnetic Ising model and spin-1 Ising model [19–21]. In Ref. [19], the spin-1 Ising system is investigated for three different types of phase transition temperatures, namely second order phase transition temperature, first order phase transition temperature, and the tricritical point. Although the numerical values of the critical exponents are different which originates from the difference of the critical exponents of the spin-1 and spin-1/2 metamagnetic Ising models, the observed critical behaviors are in agreement with each other: in both of the systems at the continuous phase transition temperatures, one of the relaxation times diverges where as the other makes a cusp. On the other hand, at the first order transition point the relaxation times show cusp and jump discontinuities. It should be stressed that for both relaxation times noncritical broad maximums which take place in the paramagnetic phase has been observed for high field values. A similar situation was also observed in [22]. Particularly decreasing and finally disappearing of the anomalies with decaying field values lead us to the suggestion that we share the same nature with the anomalies in the above mentioned paper. This attitude raises the evidence that the anomalies we have observed in the relaxation times come from the same physical origin of the anomalies in Ref. [22].

Phenomenological insight could be given into the different behaviors of the relaxation times via the corresponding eigenvectors of the secular equation, namely Eq. (11). The eigenvectors ξ_i $(i=1,2)$, are determined from the following equation:

$$\begin{bmatrix} \frac{1}{\tau_i} + \gamma_m A - \gamma B & \gamma C - \gamma_m B \\ \gamma A - \gamma_s B & \frac{1}{\tau_i} - \gamma B + \gamma_s C \end{bmatrix} \begin{bmatrix} \xi_{(i)1} \\ \xi_{(i)2} \end{bmatrix} = 0, \quad (22)$$

where $\frac{1}{\tau_i}$ are the eigenvalues given by Eq. (12). If we take $\xi_{(i)1}=1$, we obtain

$$\xi_{(i)2} = \frac{\frac{1}{\tau_i} + \gamma_m A + \gamma B}{\gamma_m B - \gamma C} \quad (23)$$

or

$$\xi_{(i)2} = \frac{\gamma_s B - \gamma A}{\frac{1}{\tau_i} - \gamma B + \gamma_s C}. \quad (24)$$

Consequently, the corresponding eigenvectors are

$$\xi_{(i)} = \begin{bmatrix} 1 \\ \xi_{(i)2} \end{bmatrix}. \quad (25)$$

Having found the relaxation times now we can determine the normal coordinates associated with the negative inverses of these relaxation times. Diagonalizing the system of equations (10) one finds

$$\begin{bmatrix} \dot{W}_1 \\ \dot{W}_2 \end{bmatrix} = - \begin{bmatrix} \frac{1}{\tau_1} & 0 \\ 0 & \frac{1}{\tau_2} \end{bmatrix} \begin{bmatrix} W_1 \\ W_2 \end{bmatrix}, \quad (26)$$

where W_1 and W_2 are the normal coordinates. Using Eq. (25) we obtain W_1 and W_2 as follows:

$$W_1 = (m - m_0) + \frac{1/\tau_1 + \gamma_m A + \gamma B}{\gamma C - \gamma_m B}(s - s_0),$$

$$W_2 = (m - m_0) + \frac{1/\tau_2 + \gamma_m A + \gamma B}{\gamma C - \gamma_m B}(s - s_0). \quad (27)$$

The values of the relaxation times given above indicate that for lower field values, in other words, when a second order phase transition takes place in the vicinity of the critical point, τ_1 remains finite whereas τ_2 diverges. In this case, from Eq. (27) we conclude that in the neighborhood of a second order phase transition the amplitude of the first normal coordinate W_1 is much smaller than the second normal coordinate W_2. On the other hand, for first order phase transition, the second normal coordinate W_2 decays more than the W_2 in the case of the second order phase transition, because τ_2 still increases rapidly but does not approach infinity. However, the value of τ_1 at the phase transition point is very little effected from the order of the transition. That is to say, W_1 represents similiar behavior for continuous and disconti-

nous phase transitions. Finally, using Eq. (27) staggered and total magnetizations can be written as follows:

$$m = m_0 + \frac{\tau_2\tau_1}{\tau_1 - \tau_2}\left\{\left[\frac{1}{\tau_2} + \frac{1}{2}(\gamma_m A - \gamma B)\right]W_1 - \left[\frac{1}{\tau_1} + (\gamma_m A - \gamma B)\right]W_2\right\},$$

$$s = s_0 + \frac{\tau_2\tau_1}{\tau_1 - \tau_2}(\gamma_m B - \gamma C)(W_1 - W_2). \quad (28)$$

Equations (28) show that the relaxation of the total and staggered magnetization is characterized by both relaxation times τ_1 and τ_2, since the time dependence of both W_1 and W_2 are characterized by τ_1 and τ_2, respectively. On the other hand, since τ_2 approaches infinity for second order phase transition points, both of the order parameters given by Eq. (28) experience critical slowing down near these points. Similar behaviors have also been obtained in the theory of relaxation of the spin-1 Ising model [19].

V. SUMMARY AND DISCUSSIONS

In this paper, we have studied the dynamics of the iron group dihalides via the metamagnetic spin-1/2 Ising model bearing competing interactions by means of Onsager's irreversible thermodynamics. First, we obtained the free energy of the system within the molecular field theory approximation and examined the behavior of the metamagnetic Ising model. Then, we calculated the Gibbs free energy production that is produced in the irreversible process. After that, the time derivatives of staggered and total magnetization are treated as fluxes conjugate to their appropriate forces in the sense of Onsager's theory. The kinetic equations are obtained by introducing the phenomenological kinetic coefficients that satisfy the Onsager's reciprocal relation. The solution of these equations near equilibrium states is given by two relaxation times which describe the nonequilibrium behavior in the cooperative system. The behavior of these relaxation times is determined as a function of temperature. The results are summarized as follows: one of the relaxation times ($\tau_1 = 1/2$) scarcely varies with temperature in the metamagnetic phase; it increases slightly just below and above all the phase transition temperatures. It should be noted that cusps are observed for the critical and multicritical behaviors of τ_1 with $\lambda_1' = 1/2$, whereas tricritical behavior of the same relaxation time is given with $\lambda_1' = 1/4$. On the other hand, a jump discontinuity ($\lambda_1' = 0.0$) is observed for the first order behavior of τ_1. The other relaxation time (τ_2) increases rapidly with increasing temperature and tends to infinity near the second and the higher order phase transition points as $(T_c - T)^{-1/2}$ and at the tricritical point as $(T_c - T)^{-1/4}$, but it has a sharp cusp with $\lambda_2' = 1/2$ at the first order transition point in the metamagnetic phase. However it is worth noting that on the other hand, for the first order transition both relaxation times show noncritical broad maximums for field values which are very close to its critical value ($H_c = z_1|J_1|$) where the staggered magnetization vanishes.

In addition, we also give a phenomenological insight for the different behavior of the relaxation times via the corresponding eigenvectors of the secular equation.

ACKNOWLEDGMENTS

We gratefully acknowledge useful discussions and conversations with R. Erdem, Gaziosmanpasa University, and A. Kabakcioglu, Koc University. Moreover, one of the authors would like to thank the Condensed Matter and Statistical Physics Section of The Abdus Salam International Centre for Theoretical Physics for their hospitality during a period of several weeks in which this work was carried out.

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