Discovery of a spin-singlet ground state with an energy gap in $CaCuGe_2O_6$

Yoshitaka Sasago, Masashi Hase, and Kunimitsu Uchinokura
Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Masashi Tokunaga and Noboru Miura
Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan
(Received 14 October 1994; revised manuscript received 17 April 1995)

The magnetic properties of $CaCuGe_2O_6$, a cuprate related to the spin-Peierls material $CuGeO_3$, were studied. The magnetic susceptibility and the magnetization curve were measured. They revealed that this compound has a spin-singlet ground state and a finite energy gap between the ground and excited states. We discuss the origin of such a property of $CaCuGe_2O_6$.

I. INTRODUCTION

Recently quantum spin systems with both a spin-singlet ground state and a finite energy gap have attracted much attention. For example, since its discovery by Hase, Terasaki, and Uchinokura,[1] the spin-Peierls transition in $CuGeO_3$ has been studied energetically and various properties of this cuprate have been reported.[1–9] The discovery of spin ladder systems such as $(VO)_2P_2O_7$ (Refs. 10–12) and $SrCu_2O_3$ (Refs. 13–16) is also a recent marked development in the field of quantum spin systems.

Inspired by the discovery of the spin-Peierls transition in $CuGeO_3$, we directed our attention to germanates and silicates with magnetic ions. These compounds have various crystal structures because of chemical properties of Ge^{4+} and Si^{4+}, which lead to various magnetic networks. Thus there is a possibility to find novel magnetic systems with interesting magnetic properties in these compounds. There have been a few studies of the magnetic properties of germanates and silicates. For example, $CaFeSi_2O_6$,[17] $NaFeSi_2O_6$,[18] and $LiFeSi_2O_6$ (Ref. 18) exhibit Néel order at 35, 5, and 19.5 K, respectively. However, to the best of our knowledge, there have been few reports of germanates and silicates,[19] except for $CuGeO_3$, which have low-dimensional antiferromagnetic (AF) quantum-spin systems.

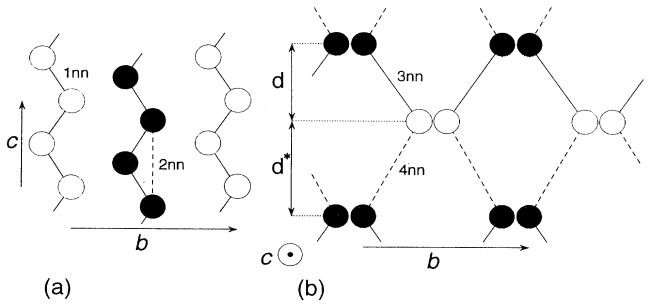

FIG. 1. Schematic Cu configuration in $CaCuGe_2O_6$. Both open and solid circles represent Cu sites. (a) The projection of two neighboring b-c planes including zigzag chains. Open and solid circles are located on different planes. The 1NN and the 2NN Cu pairs are denoted by solid and dashed lines, respectively. (b) The projection to the plane perpendicular to the c axis. Both • • and ○ ○ denote zigzag chains parallel to the c axis. The 3NN and 4NN Cu pairs are indicated by solid and dashed lines, respectively. The distance between two neighboring b-c planes alternates, i.e., $d \neq d^*$.

Among many germanates and silicates with magnetic ions, we decided to study the magnetic properties of $CaCuGe_2O_6$. The magnetism is mainly determined by spins on Cu^{2+} ions ($S = 1/2$). In addition, this compound has a simpler crystal structure than most of other germanates and silicates. The space-group symmetry is $P2_1/c$ (No. 14 of Ref. 20) at room temperature.[21] The lattice parameters are $a = 10.198$ Å, $b = 9.209$ Å, $c = 5.213$ Å, $\beta = 105.73°$, and $Z = 4$. We show a schematic Cu configuration in Fig. 1. Cu ions form zigzag chains along the c axis [Fig. 1(a)]. Figure 1(b) represents the projection of zigzag chains on the plane perpendicular to the c axis. The first-nearest-neighbor (1NN) and the second-nearest-neighbor (2NN) Cu pairs are located in the same zigzag chain as is seen in Fig. 1(a). The third-nearest-neighbor (3NN) and the fourth-nearest-neighbor (4NN) pairs are indicated by solid and dashed lines, respectively, in Fig. 1(b). The distances between two Cu ions in 1NN, 2NN, 3NN, and 4NN pairs are 3.072, 5.213, 5.549, and 6.213 Å, respectively. It should be noted that one Cu ion has two 1NN Cu's, two 2NN Cu's, *one* 3NN Cu, and *one* 4NN Cu. The distance between two neighboring b-c planes containing zigzag chains alternates. The two distances are 4.462 (d) and 5.354 (d^*) Å [Fig. 1(b)].

In the present study, we have discovered the existence of a spin-singlet ground state with an energy gap in $CaCuGe_2O_6$. This discovery is very interesting partly because only a few cuprates have such a magnetic property and also because the detailed magnetic properties of this material are distinguished from those of other materials with a spin-singlet ground state and an energy gap.

II. EXPERIMENT

Single crystals of $CaCuGe_2O_6$ were grown by the self-flux method. Starting materials are $CaCO_3$ (purity of 99.9%), CuO (99.99%), and GeO_2 (99.999%). A single crystal was not large enough for the measurements of the susceptibility and the magnetization. Therefore we pulverized several crystals and used the powdered samples for the measurements. No impurity phases were detected in the x-ray diffraction patterns of the powdered $CaCuGe_2O_6$. On the other hand, pure polycrystalline $CaCuGe_2O_6$ was not obtained by a solid-state reaction method around 1000 °C from the stoichiometric mixture. The impurity phase of sintered samples was $CuGeO_3$. It seems that $CuGeO_3$ is stabler than $CaCuGe_2O_6$ around 1000 °C. We measured the temperature (T) dependence of the magnetic susceptibility [$\chi(T)$] and the magnetic-field (H) dependence of the magnetization [$M(H)$] by a superconducting quantum interference device (SQUID) magnetometer and by an induction method in the increasing pulsed field, respectively. In order to determine the g value (g) of the localized $S = 1/2$ spins on Cu^{2+} ions, the electron spin resonance (ESR) spectrum was measured at 8.99 GHz.

III. EXPERIMENTAL RESULTS AND DISCUSSION

We show $\chi(T)$ in 0.01 T in the field-cooling process between 4.2 and 300 K by solid circles in Fig. 2. There are no meaningful differences between the data in zero-field-cooling and field-cooling processes. The most prominent characteristic is that $\chi(T)$ drops towards 0 below 40 K with decreasing T. It means that the ground state is spin singlet and that there exists a finite energy gap between the ground and excited states. We emphasize that there is no phase transition between 4.2 and 300 K. Therefore, unlike the spin-Peierls transition in $CuGeO_3$,[1] the spin-singlet ground state with a finite energy gap of $CaCuGe_2O_6$ is not induced by any phase transition, but it is intrinsic to $CaCuGe_2O_6$. A small increase of $\chi(T)$ was observed below 10 K, which is due to some magnetic impurities and/or defects of Cu^{2+} ions in $CaCuGe_2O_6$. On the other hand, $\chi(T)$ has a broad maximum around 40 K, which is the characteristic property of low-dimensional AF spin systems.

Before showing the experimental result of high-field $M(H)$ of $CaCuGe_2O_6$, we briefly summarize the properties of the magnetization of the spin system with both a spin-singlet ground state and a finite energy gap. The existence of the energy gap can be more directly confirmed from the magnetization at low temperatures. The magnetization of the above-mentioned spin system is expected to exhibit two characteristic nonzero critical magnetic fields at 0 K.[22] The magnetization becomes finite above the lower critical field (H_{c1}), where the Zeeman energy exceeds the energy gap, and is saturated above the higher critical field. As long as the energy gap is much larger than T, we can observe the existence of the critical fields even if T is not 0 K.

The thick solid curve in Fig. 3 represents $M(H)$ of $CaCuGe_2O_6$ up to 40 T at 4.2 K. There is a drastic increase of $M(H)$ above 30 T, which means the existence of the energy gap. Below 20 T the magnitude of $M(H)$ is very small and the shape of the curve is convex up [$d^2M(H)/dH^2 < 0$]. In this range of H, $M(H)$ is mainly due to magnetic impurities and/or defects and the contribution from $CaCuGe_2O_6$ is little. We have not observed the saturation of $M(H)$.

From the ESR spectrum of the powdered sample at room temperature, we evaluated the g value of $S = 1/2$ spins on Cu^{2+} ions as 2.07. This value is close to the usual one of Cu^{2+} spins in ordinary cuprates such as $CuGeO_3$.[23]

Now we will consider the origin of the spin-singlet ground state with the energy gap observed in $CaCuGe_2O_6$. We start from the discussion of $\chi(T)$. In order to analyze the susceptibility quantitatively, we eliminated the Curie-like term in $\chi(T)$ as in Fig. 2. It is assumed that the spins due to impurities and/or defects of Cu^{2+} ions are isolated spins. Thus the data below 10 K were fitted to C/T. The result is shown as the dashed curve in Fig. 2. The value of C was evaluated to be 9.3×10^{-3} emu K/mol, which means that about 3% of Cu^{2+} spins are isolated spins.[24] We assumed that the g value of the spins due to impurities and/or defects is 2.07. The data of $\chi(T) - C/T$ [$\equiv \chi_t(T)$] are represented by open circles.

We compare $\chi_t(T)$ with the susceptibility of isolated AF dimers. The spin system consisting of isolated AF dimers is the simplest in systems with both a spin-singlet ground state and a finite energy gap. The Hamiltonian is expressed as

$$H_{\text{dimer}} = 2J \sum_{j=1}^{N} \mathbf{S}_{j,1} \cdot \mathbf{S}_{j,2} - g\mu_B H \sum_{j=1}^{N} (S^z_{j,1} + S^z_{j,2}). \quad (1)$$

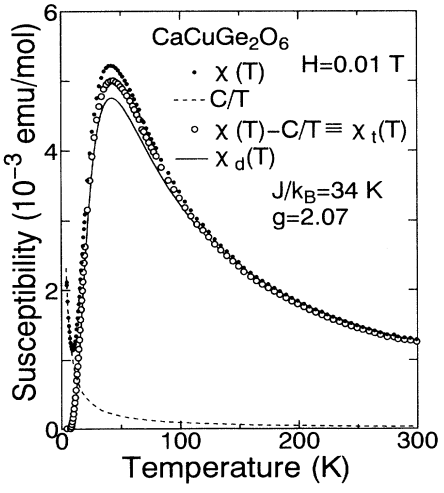

FIG. 2. The temperature dependence of the magnetic susceptibility measured in 0.01 T. Solid circles, dashed curve, open circles, and solid curve represent the measured susceptibility [$\chi(T)$], the susceptibility due to impurities and/or defects [C/T], $\chi_t(T) \equiv \chi(T) - C/T$, and the theoretical susceptibility [$\chi_d(T)$], respectively.

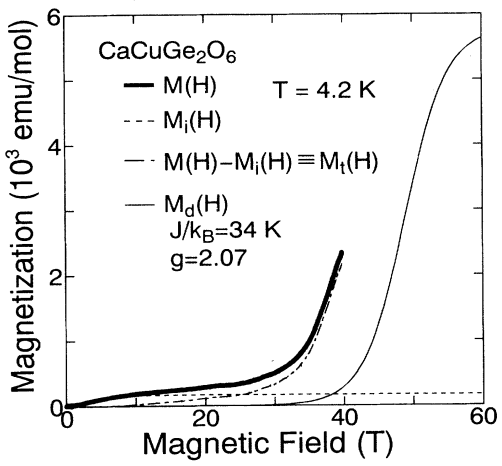

FIG. 3. The magnetization of $CaCuGe_2O_6$ at 4.2 K. Thick solid, dashed, dash-dotted, and thin solid curves represent the measured magnetization $[M(H)]$, the magnetization due to impurities and/or defects $[M_i(H)]$, $M_t(H) \equiv M(H) - M_i(H)$, and the theoretical magnetization $[M_d(H)]$, respectively.

The quantities of J (> 0), N, $\mathbf{S}_{j,i}$ $(i = 1$ or $2)$, and μ_B denote the AF exchange interaction, the number of the dimers, the spin operator of $S = 1/2$, and the Bohr magneton, respectively. After a brief calculation, we obtain the susceptibility of this system $[\chi_d(T)]$,

$$\chi_d(T) = \frac{2N(g\mu_B)^2}{k_BT[\exp(2J/k_BT) + 3]}, \quad (2)$$

where k_B is the Boltzmann constant. In Eq. (2), only J is an unknown parameter. We determined the value of J so as to make the temperatures at maximum $\chi_t(T)$ and $\chi_d(T)$ coincide with each other. As a result, J was estimated to be 34 K. The curve of $\chi_d(T)$ is shown by the solid curve in Fig. 2.

The theoretical curve $[\chi_d(T)]$ agrees well with $\chi_t(T)$ qualitatively. This agreement indicates that the magnetic properties of $CaCuGe_2O_6$ can be explained approximately by the spin system with isolated AF dimers. As is seen around 40 K, a quantitative discrepancy exists between $\chi_t(T)$ and $\chi_d(T)$. Especially it should be emphasized that the maximum value of $\chi_t(T)$ is larger than that of $\chi_d(T)$. This discrepancy is most probably due to interdimer interactions.

Now we consider which Cu pairs can constitute AF dimers. On the basis of the Cu configuration in Fig. 1, it is concluded that the 3NN Cu pair (or presumably the 4NN Cu pair) leads to the AF dimer. In other words, the exchange interaction in such a pair is dominant, and other interactions are very small. As was already mentioned, the 1NN (the 2NN) bonds constitute the uniform zigzag (linear) chains along the c axis and therefore cannot constitute AF dimers. At first glance, it seems strange that the 1NN interaction is much smaller than the 3NN or the 4NN one. However, as is well known, an exchange interaction between two spins is not determined solely by the distance between the two spins. For example, in $Cu(NO_3)\cdot 2.5H_2O$, the 2NN interaction is dominant.[22] However, consideration of the crystal structure of $CaCuGe_2O_6$ leads to possible existence of the interdimer interactions.

In the following paragraphs, we discuss $M(H)$. As was done in $\chi(T)$, we eliminated the magnetization of isolated $S = 1/2$ spins leading to the Curie term in $\chi(T)$. This magnetization $[M_i(H)]$ was calculated with $C = 9.3 \times 10^{-3}$ emu K/mol obtained in the analysis of the susceptibility, and $M_i(H)$ is represented by the dashed curve in Fig. 3. It is noted that $M(H)$ coincides with $M_i(H)$ below 10 T. We also show $M(H) - M_i(H)$ $[\equiv M_t(H)]$ by the dash-dotted curve. We compared $M_t(H)$ with the magnetization of isolated AF dimers $[M_d(H)]$. The quantity of $M_d(H)$ is calculated as follows:

$$M_d(H) = \frac{2Ng\mu_B \sinh(g\mu_BH/k_BT)}{1 + \exp(2J/k_BT) + 2\cosh(g\mu_BH/k_BT)}. \quad (3)$$

The thin solid curve represents $M_d(H)$ with $g = 2.07$ and $J/k_B = 34$ K.

Although $M_t(H)$ and $M_d(H)$ have a similar H dependence, $M_t(H)$ does not agree quantitatively with $M_d(H)$. Especially the field above which the magnetization rapidly increases in $M_t(H)$ is about 9 T lower than that in $M_d(H)$. The value of H_{c1} of the AF dimer system is calculated to be 48.9 T. Therefore we think that H_{c1} of $CaCuGe_2O_6$ is about 40 T $[\sim 48.9 - 9$ (T)]. The discrepancy between $M_t(H)$ and $M_d(H)$ should be attributed to interdimer interactions. Since the interdimer interactions are much weaker than the intradimer ones, low-field properties such as the susceptibility are insensitive to the interdimer interactions.[25] Accordingly $\chi_t(T)$ agrees well with $\chi_d(T)$. On the contrary, high-field properties are sensitive to the interdimer interactions[25] and the above-mentioned discrepancy in the magnetization appears.

We comment on candidates of interdimer interactions and compare the magnetic properties of $CaCuGe_2O_6$ with those of other materials with interacting AF dimers. Three kinds of interdimer interactions can be considered. We will give three models of interdimer interactions. We repeat that either the 3NN or the 4NN interaction is dominant. First, if neither the 3NN nor the 4NN interaction is negligible, which means that either the 3NN or the 4NN interaction is the interdimer one, $CaCuGe_2O_6$ has zigzag chains with alternating exchange interactions [Fig. 4(a)]. In the case that the interdimer interaction is AF, there are several theoretical and experimental studies and accordingly we can compare our experimental results with them.[22,25–27] Treating the interdimer interaction in an alternating spin system as a perturbation, we can simply derive the energy gap between spin-singlet ground state and $S = 1$ excited state to second order in α as $E_{\rm gap} = 2J(1 - \frac{1}{16}\alpha^2 - |\frac{1}{2}\alpha + \frac{1}{4}\alpha^2|)$, where α is the ratio of interdimer interaction to J (Appendix). Considering $H_{c1} \approx 40$ T, $J = 34$ K, and $g = 2.07$, we can estimate $\alpha \approx 0.31$ and -0.44 for AF and ferromagnetic (F) interdimer interactions, respectively.[28] However it is emphasized that $\chi_t(T)$ differs much from the susceptibility of the alternating spin system with $\alpha = 0.31$.[26] Therefore we can deny the possibility that either the

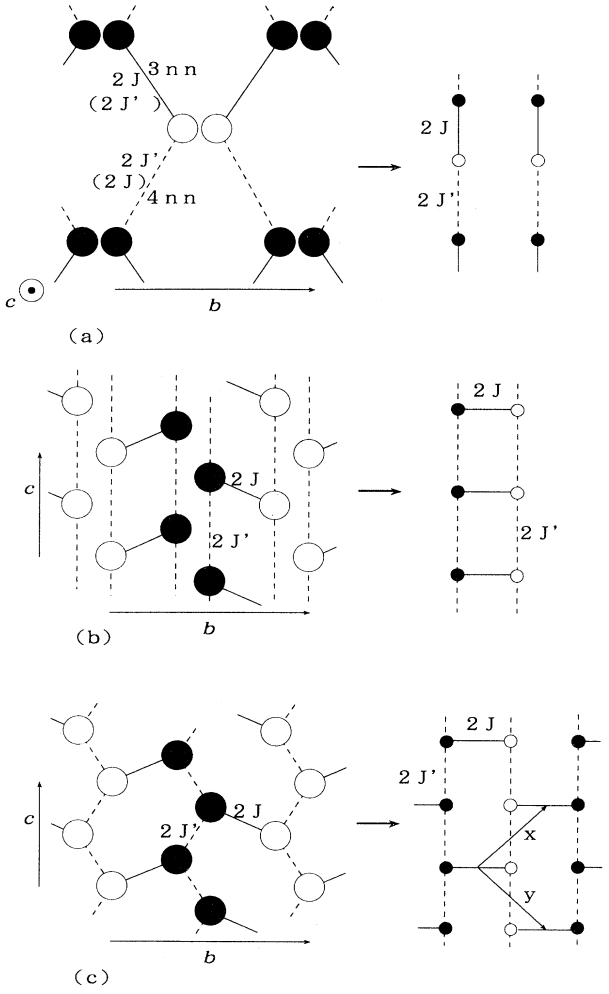

FIG. 4. The three models of the interdimer interactions. (a) The 3NN and 4NN interactions form the alternating spin system. (b) AF dimers with the 2NN interdimer interaction form spin ladder. (c) AF dimers with the 1NN interdimer interaction form the two-dimensional magnetic system. We consider the simplified lattices in the right sides in calculating the excitation energy in the Appendix.

3NN or the 4NN interaction is a dominant AF interdimer one. The present results strongly differ from those of $Cu(NO_3)_2{\cdot}2.5H_2O$, in which the magnetic susceptibility and the magnetization can be explained almost completely by the model of an alternating spin system with $\alpha = 0.27$.[22] In the case of F interdimer interactions, there is no theory about the temperature dependence of the susceptibility. We will comment on these F interdimer interactions later. Second, if the 2NN interaction is a dominant interdimer interaction, $CaCuGe_2O_6$ has double linear chains parallel to the c axis which lead to the spin ladder system such as $(VO)_2P_2O_7$ and $SrCu_2O_3$ [Fig. 4(b)]. It is noted that the spin ladder has a spin-singlet ground state with an energy gap[16,29] when both exchange interactions of leg ($J_\parallel$) and rung ($J_\perp$) are AF. In $(VO)_2P_2O_7$ (Refs. 11 and 12) and $SrCu_2O_3$,[14–16] it is reported that $J_\parallel/J_\perp$ is about 1. Assuming that $CaCuGe_2O_6$ forms the spin ladder system with AF $J_\parallel$ and $J_\perp$, we can estimate that $J_\parallel/J_\perp \approx 0.22$ from $H_{c1} \approx 40$ T with the aid of Eq. (10) in Ref. 29.[28] Similarly when $J_\parallel$ is F, we can estimate that $J_\parallel/J_\perp \approx -0.22$.[28] These values are quite different from those of $(VO)_2P_2O_7$ and $SrCu_2O_3$. We cannot conclude whether or not the susceptibility of the spin ladder system with $J_\parallel/J_\perp = 0.22$ or -0.22 agrees quantitatively with that of $CaCuGe_2O_6$ because of the absence of a theoretical result. Third, if the 1NN interaction is a dominant interdimer one, the spin system of $CaCuGe_2O_6$ can be represented as an ensemble of weakly coupled dimers confined in two neighboring b-c planes [Fig. 4(c)]. In this case, using perterbation theory to second order in β, we can estimate the energy gap as $E_{\rm gap} = 2J(1 - \frac{5}{8}\beta^2 - |\beta + \beta^2|)$, where β is the ratio of interdimer interaction to J (Appendix). Considering $H_{c1} \approx 40$ T, $J = 34$ K, and $g = 2.07$, we can estimate that $\beta \approx 0.15$ and -0.20 for AF and F interdimer interactions, respectively.[28]

In this paragraph, F interdimer interactions are considered. These interactions may explain the relation $\chi_t(T) > \chi_d(T)$ around 40 K, which does not seem to be explained by AF interdimer interactions. We now consider the following Hamiltonian which means the model of two AF dimers with interdimer interactions:

$$H_{\rm 2dimer} = 2J\sum_{j=1}^{N'}(\mathbf{S}_{j,1}{\cdot}\mathbf{S}_{j,2} + \mathbf{S}_{j,3}{\cdot}\mathbf{S}_{j,4}) + 2J'\sum_{j=1}^{N'}(\mathbf{S}_{j,2}{\cdot}\mathbf{S}_{j,3} + \mathbf{S}_{j,4}{\cdot}\mathbf{S}_{j,1}) - g\mu_B H\sum_{j=1}^{N'}(S^z_{j,1} + S^z_{j,2} + S^z_{j,3} + S^z_{j,4}), \quad (4)$$

where J (> 0), N', $\mathbf{S}_{j,i}$ ($i = 1, 2, 3$, or 4), and J' denote the intradimer (AF) interaction, the number of pairs of dimers, the spin operator of $S = 1/2$, and interdimer interaction, respectively. The expression of the susceptibility of this system is

$$\chi_{\rm 2dimer}(T) = \frac{X}{Y}, \quad (5)$$

$$X = N'(g\mu_B)^2\{10\exp(-E_2/k_BT) + 2[\exp(-E_{1A}/k_BT) + \exp(-E_{1B}/k_BT) + \exp(-E_{1C}/k_BT)]\}, \quad (6)$$

$$Y = k_BT\{5\exp(-E_2/k_BT) + 3[\exp(-E_{1A}/k_BT) + \exp(-E_{1B}/k_BT) + \exp(-E_{1C}/k_BT)] + \exp(-E_0/k_BT) + \exp(-E_{00}/k_BT)\}, \quad (7)$$

where $E_2, E_{1A}, E_{1B}, E_{1C}, E_0$, and E_{00} are $J+J', J-J', -(J-J'), -(J+J'), -J-J'+\sqrt{(J+J')^2+3(J-J')^2}$, and $-J-J'-\sqrt{(J+J')^2+3(J-J')^2}$, respectively. The values of positive and negative J' indicate AF and F interdimer interactions, respectively. This is the simplest model of interdimer interactions and we know, from the viewpoint of the symmetry of the crystal structure, that it cannot be realized in $CaCuGe_2O_6$. However, this model may show us the tendency of the effects of AF and F interdimer interactions on the susceptibility. This model corresponds to N' uniform AF rings of four spins, $2N'$ AF dimers, and N' AF dimers of $S = 1$, when $J' = J$, 0, and $-\infty$, respectively. Figure 5 shows the temperature dependence of the susceptibility of AF dimers with various values of γ $(= J'/J)$ with fixed J. In contrast with the AF interdimer interaction, the weak F interdimer interaction makes the maximum value of the susceptibility large, while the peak temperature remains almost constant. This result suggests that there exists an F interdimer interaction in $CaCuGe_2O_6$. The above-described results are exact but are based on a simpler model than the real system. On the other hand, in the case of $|J'| \ll J$, $|J'| \ll k_BT$, and $|g\mu_BH| \ll J$, the interdimer interactions can be dealt as a mean field.[30] We calculate the susceptibility by a mean-field approximation. The Hamiltonian is expressed as

$$H_m = 2J\sum_{j=1}^{N}\mathbf{S}_{j,1}\cdot\mathbf{S}_{j,2} + 2J'\sum_{\langle j,i;j',i'\rangle}\mathbf{S}_{j,i}\cdot\mathbf{S}_{j',i'} - g\mu_BH\sum_{j=1}^{N}(S^z_{j,1}+S^z_{j,2}), \quad (8)$$

where $\sum_{\langle j,i;j',i'\rangle}$ denotes summation over the interacting $\mathbf{S}_{j,i}$ and $\mathbf{S}_{j',i'}$ (interdimer interaction). In addition we define the number of spins interacting with interdimer interactions with one $\mathbf{S}_{j,i}$ as n. In the case of the alternating spin system, spin ladder, weakly coupled dimers confined in two neighboring b-c planes, n's are 1, 2, and 2, respectively. In the model of Eq. (4), n is considered to be 1. The susceptibility calculated by the mean-field approximation is expressed as

$$\chi_m(T) = \frac{2N(g\mu_B)^2}{k_BT[\exp(2J/k_BT)+3]+2J'n}. \quad (9)$$

The mean-field results of the susceptibility also support F interdimer interactions in $CaCuGe_2O_6$, since $\chi_m(T)$ with $J' < 0$ is larger than that with $J' = 0$. In Fig. 6, we compare $\chi_t(T)$ with $\chi_m(T)$ and obtained the value of $J'n/J$. If the Curie term in Fig. 2 comes completely from the defects of the Cu sites, we should fit $\chi_m(T)$ to $\chi_t(T)/0.94$ (Ref. 24) and the resultant value of $J'n/J$ is about -0.5. On the other hand, if we fit $\chi_m(T)$ to $\chi_t(T)$, it is estimated as about -0.2. Thus the interpretation of the Curie term in $\chi(T)$ strongly influences the estimation of $J'n/J$ within the mean-field approximation. In order to determine the type of interdimer interaction we compared these values with those estimated from the magnetization: $J'n/J = -0.44, -0.44$, and -0.40 for alternating spin system, spin ladder, and two-dimensional magnetic system, respectively. However, since the differences among these three values are quite small, we did not succeed. In the case of $|J'| \approx J$, the validity of the mean-field approximation should be reconsidered. In Fig. 5, we also show $\chi_m(T)$ in the model of Eq. (4). In this model, the relation $n = 1$ holds. For small values of $|J'|$ such as the case of $J' = -0.2J$, the exact susceptibility and $\chi_m(T)$ agree very well. But for the larger value of $|J'|$, the discrepancy is remarkable around the broad maximum of the susceptibility. Not only for this simpler model but also for more general models, such a tendency seems to be expected. For these reasons, it is difficult to

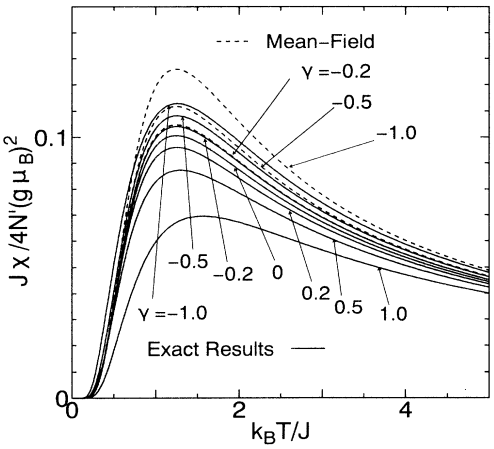

FIG. 5. Magnetic susceptibility of AF dimers with F interdimer interactions [referred to Eq. (4)]. The solid and dashed lines denote the exact results and $\chi_m(T)$'s [referred to Eq. (9)]. The value of γ denotes the degree of the interdimer interaction ($\gamma = J'/J$). We can see that F interdimer interactions make the maximum value of the susceptibility large.

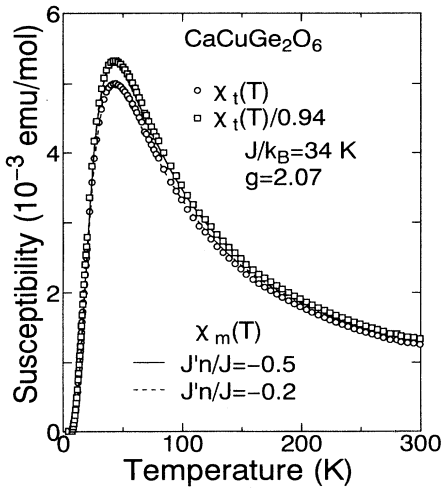

FIG. 6. Comparison between $\chi_t(T)$ with $\chi_m(T)$. Open circles and open squares denote $\chi_t(T)$ and $\chi_t(T)/0.94$, respectively. The solid and dashed lines denote $\chi_m(T)$'s with $J'n/J = -0.2$ and -0.5, respectively.

estimate the value of $J'n$ accurately. We only emphasize that the presence of the F interdimer interactions can explain the temperature dependence of the susceptibility of $CaCuGe_2O_6$. From the viewpoint of the crystal structure, this F interdimer interaction is considered to be in the 1NN Cu-Cu bond, because the Cu-O-Cu angle in this bond is nearly 90° (Ref. 21). We do not fit $M_t(T)$ with the mean-field magnetization, because the mean-field treatment is not suitable at low temperatures and in high magnetic field. The magnetic properties of the system at low temperatures and in high magnetic field are expected to reflect the details of the interdimer interactions, in contrast to those at high temperature and therefore the deviations from the mean-field results become very serious. Similarly it is not meaningful to compare $M_t(H)$ with the magnetization of the simple model [Eq. (4)].

Last, we emphasize that several magnetic systems with a spin-singlet ground state with a finite energy gap have been studied as AF dimers with some kinds of interdimer interactions. The above-mentioned alternating spin system and spin ladder are examples of such systems. In addition, we can regard even the Haldane gap system of $S = 1$ (Refs. 31 and 32) as AF dimers with infinitely strong F interdimer interactions.[33,34] It is expected that detailed studies of interdimer interactions in $CaCuGe_2O_6$ will lead us to a new kind of magnetic system.

IV. SUMMARY

We measured the temperature dependence of the magnetic susceptibility and the magnetic-field dependence of the magnetization of powdered $CaCuGe_2O_6$. The susceptibility reduces rapidly to 0 below 40 K with decreasing T, and the magnetization at 4.2 K increases drastically above 30 T. These results mean the existence of the spin-singlet ground state with a finite energy gap. It should be emphasized that very few cuprates have such a magnetic property. The magnetism of $CaCuGe_2O_6$ can be explained by the spin system consisting of antiferromagnetic dimers with weak interdimer interactions. The dimers are assigned to either the third-nearest-neighbor or presumably the fourth-nearest-neighbor Cu pairs. The interdimer interactions of $CaCuGe_2O_6$ are considered to be ferromagnetic, which is different from the previously reported antiferromagnetic dimers with interdimer interactions.

ACKNOWLEDGMENTS

We would like to thank M. Izumi of Tokyo University of Mercantile Marine for the ESR measurement. We would also thank I. Terasaki of Superconductivity Research Laboratory, International Superconductivity Technology Center, for the discussion at an early stage of this study.

APPENDIX: DERIVATION OF THE ENERGY GAP

We describe the derivation of the energy gaps of the alternating spin system [Fig. 4(a)] and the two-dimensional magnetic system [Fig. 4(c)], using perturbation theory to second order. We consider the Hamiltonian as

$$H = 2J \sum_{j=1}^{N} \mathbf{S}_{j,1} \cdot \mathbf{S}_{j,2} + H_I \ , \tag{A1}$$

where the first term on the right hand and the second one are intradimer and interdimer interactions. We deal the latter as a perturbation. The unperturbed ground state is the simple product of singlet states between spins at $(j,1)$ and $(j,2)$ sites. Using perturbation theory to second order, we calculate the ground-state energies as

$$E_0 = -JN \left(\frac{3}{2} + \frac{3}{16}\alpha^2 \right) \tag{A2}$$

and

$$E_0 = -JN \left(\frac{3}{2} + \frac{3}{8}\beta^2 \right) \tag{A3}$$

for the alternating spin system and the two-dimensional magnetic system, respectively. The unperturbed first excited states are $3N$-fold degenerate. Using perturbation theory to second order, we obtain the energies of the triplet or $S = 1$ states as

$$E(k) = -JN \left(\frac{3}{2} + \frac{3}{16}\alpha^2 \right) + 2J \left[1 - \frac{1}{16}\alpha^2 - \left(\frac{1}{2}\alpha + \frac{1}{4}\alpha^2 \right) \cos k \right] \tag{A4}$$

and

$$E(k_x, k_y) = -JN \left(\frac{3}{2} + \frac{3}{8}\beta^2 \right) + 2J \left[1 - \frac{5}{8}\beta^2 - \frac{1}{2}(\beta + \beta^2)(\cos k_x + \cos k_y) \right] \tag{A5}$$

for the alternating spin system and the two-dimensional magnetic system, respectively, where k and (k_x, k_y) denote the wave vector. All the energy levels are threefold degenerate [$S_z = -1$, 0, and +1]. In the case of the alternating spin system, the excitation energy has a minimum at $k = 0$ for $\alpha > 0$ and at $k = \pi$ for $-2 < \alpha < 0$. The energy gap between the ground and the first excited states is

$$E_{\text{gap}} = 2J \left(1 - \frac{1}{16}\alpha^2 - \left| \frac{1}{2}\alpha + \frac{1}{4}\alpha^2 \right| \right) . \tag{A6}$$

In the case of a two-dimensional magnetic system, the excitation energy has a minimum at $(k_x, k_y) = (0, 0)$ for $\beta > 0$ and at $(k_x, k_y) = (\pi, \pi)$ for $-1 < \beta < 0$. The energy gap is

$$E_{\text{gap}} = 2J \left(1 - \frac{5}{8}\beta^2 - |\beta + \beta^2| \right) . \tag{A7}$$

[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[2] M. Hase, I Terasaki, K. Uchinokura, M. Tokunaga, N. Miura, and H. Obara, Phys. Rev. B **48**, 9616 (1993).
[3] H. Kuroe, K. Kobayashi, T. Sekine, M. Hase, Y. Sasago, I. Terasaki, and K. Uchinokura, J. Phys. Soc. Jpn. **63**, 365 (1994).
[4] J. Kikuchi, T. Yasuoka, M. Hase, Y. Sasago, and K. Uchinokura, J. Phys. Soc. Jpn. **63**, 872 (1994).
[5] J. P. Pouget, L. P. Regnault, M. Ain, B. Hennion, J. P. Renard, P. Veillet, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. **72**, 4037 (1994).
[6] K. Hirota, D. E. Cox, J. E. Lorenzo, G. Shirane, J. M. Tranquada, M. Hase, K. Uchinokura, H. Kojima, Y. Shibuya, and I. Tanaka, Phys. Rev. Lett. **73**, 736 (1994).
[7] J. E. Lorenzo, K. Hirota, G. Shirane, J. M. Tranquada, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, Phys. Rev. B **50**, 1278 (1994).
[8] T. Hamamoto, N. Adachi, G. Kido, M. Hase, Y. Sasago, and K. Uchinokura, J. Phys. Soc. Jpn. **63**, 1218 (1994).
[9] M. Hase, I. Terasaki, Y. Sasago, K. Uchinokura, and H. Obara, Phys. Rev. Lett. **71**, 4059 (1993).
[10] D. C. Johnston, J. W. Johnson, D. P. Goshorn, and A. J. Jacobson, Phys. Rev. B **35**, 219 (1987).
[11] T. Barnes and J. Riera, Phys. Rev. B **50**, 6817 (1994).
[12] R. S. Eccleston, T. Barnes, J. Brody, and J. W. Johnson, Phys. Rev. Lett. **73**, 2626 (1994).
[13] M. Azuma, Z. Hori, M. Takano, K. Ishida, and Y. Kitaoka, Phys. Rev. Lett. **73**, 3463 (1994).
[14] T. M. Rice, S. Gopalan, and M. Sigrist, Europhys. Lett. **23**, 445 (1993).
[15] M. Sigrist, T. M. Rice, and F. C. Zhang, Phys. Rev. B **49**, 12 058 (1994).
[16] S. Gopalan T. M. Rice, and M. Sigrist, Phys. Rev. B **49**, 8901 (1994).
[17] J. M. D. Coey and S. Ghose, Solid State Commun. **53**, 143 (1985).
[18] E. Baum, W. Treutmann, M. Behruzi, W. Lottermoser, and G. Amthauer, Z. Kristallogr. **183**, 273 (1988).
[19] M. Wintenberger, G. Andre, and M. F. Gardette, Solid State Commun. **87**, 309 (1993).
[20] Vol. A of *International Tables for Crystallography, Space-Group Symmetry*, 3rd revised ed., edited by T. Hahn (Kluwer Academic Publishers, Dordrecht, 1992).
[21] M. Behruzi, K.-H. Breuer, and W. Eysel, Z. Kristallogr. **176**, 205 (1986).
[22] J. C. Bonner, S. A. Friedberg, H. Kobayashi, D. L. Meier, and H. W. J. Blöte, Phys. Rev. B **27**, 248 (1983).
[23] G. A. Petrakovskii, K. A. Sablina, A. M. Vorotynov, A. I. Kruglik, A. G. Klimenko, A. D. Balayev, and S. S. Aplesnin, Sov. Phys. JETP **71**, 772 (1990).
[24] If we assume that the Curie term comes completely from the defects of Cu sites, the susceptibility from 1 mol stoichiometric $CaCuGe_2O_6$ is expected to be $(1/0.94)\chi_t(T)$. where we derive the value 0.94 from $1-2\times0.03$ with the aid of the estimated density of defects, 0.03.
[25] K. M. Diederix, H. W. J. Blöte, J. P. Groen, T. O. Klaassen, and N. J. Poulis, Phys. Rev. B **19**, 420 (1979).
[26] J. C. Bonner, H. W. J. Blöte, J. W. Bray, and I. S. Jacobs, J. Appl. Phys. **50**, 1810 (1979).
[27] J. C. Bonner and H. W. J. Blöte, Phys. Rev. B **25**, 6959 (1982).
[28] Our estimation is based on the assumption that the relation $E_{\rm gap} = g\mu_B H_{c1}$ holds. It means that the lowest $S = 1$ excited state becomes a ground state earlier than other excited states. In principle, there is a possibility that with increasing magnetic field the excited state with higher spin becomes a ground state earlier than the lowest $S = 1$ excited state. We think that this assumption does not lead to a fatal error, since in $CaCuGe_2O_6$ the interdimer interaction can be considered weak.
[29] T. Barnes, E. Dagotto, J. Riera, and E. S. Swanson, Phys. Rev. B **47**, 3196 (1993).
[30] D. J. Scalapino, Y. Imry, and P. Pincus, Phys. Rev. B **11**, 2042 (1975).
[31] F. D. M. Haldane, Phys. Lett. **93A**, 469 (1983).
[32] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
[33] K. Hida, Phys. Rev. B **45**, 2207 (1992).
[34] M. Kohmoto and H. Tasaki. Phys. Rev. B **46**, 3486 (1992).