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Spin-1/2 quantum antiferromagnetic chains with adjustable superexchange interactions found in $BaCu_2(Si_{1-x}Ge_x)_2O_7$

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Abstract

Synthesis, structure, and magnetic properties of a novel one-dimensional spin-1/2 quantum antiferromagnetic (AF) system $BaCu_2(Si_{1-x}Ge_x)_2O_7$ ($0 \le x \le 1$) are reported. Contained in this system are corrugated CuO_3 chains made of corner-sharing CuO_4 squares, with the dominant exchange interactions being found to change almost linearly with the composition between 290 K ($x=0$) and 580 K ($x=1$). Anomalies in susceptibility and specific heat, indicative of the occurrence of a long-range AF ordering, are observed at 8.9 K ($x=0$) and 8.6 K ($x=1$). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Quantum spin system; Cupric oxide; CuO_2 chain

1. Introduction

One dimensional (1D) Heisenberg antiferromagnetic (HAF) spin systems are known to exhibit various exotic magnetism caused by large quantum fluctuations which suppress an ordinary long-range order (LRO). Recent extensive studies on 1D cupric oxides have revealed interesting properties such as the spin-Peierls transition in $CuGeO_3$ [1] and the spin-charge separation in $SrCuO_2$ [2].

Two kinds of Cu–O chains made of CuO_4 squares are known; a corner-sharing chain as seen in Sr_2CuO_3 and $SrCuO_2$, and an edge-sharing chain as in many other cupric oxides such as $CuGeO_3$, Li_2CuO_2, $(Ca,Sr)_{14}Cu_{24}O_{41}$, and $Ca_{1-x}CuO_2$. The former type exhibits a relatively large AF interaction J of the order of 10^3 K due to a strong Cu 3d–O 2p mixing in the linear Cu–O–Cu bond, while the Cu–O–Cu bond bent to ~90° can be either AF or ferromagnetic (F). According to a theoretical study by Mizuno et al. [3], the nearest neighbor (n.n.) interaction J_1 depends sensitively on the bond angle θ in such a way that $J_1/k_B \sim -100$ K (F) for Li_2CuO_2 ($\theta \sim 94°$) and 140 K (AF) for $CuGeO_3$ ($\theta = 99°$). In contrast, the second n.n. interaction J_2 is always AF as 62 K for Li_2CuO_2 and 18 K for $CuGeO_3$ for example. On the other hand, the bond-angle dependence of J for a corner-sharing chain has not yet been studied experimentally nor theoretically. This is mainly because appropriate model compounds have not been studied experimentally.

Here we report on $BaCu_2Si_2O_7$, $BaCu_2Ge_2O_7$, and their solid solutions $BaCu_2(Si_{1-x}Ge_x)_2O_7$ which contain unique corner-sharing CuO_3 chains bent to ~130°. The crystal structure of $BaCu_2Si_2O_7$ was solved by Janczak et al. using the Rietveld analysis of the powder X-ray diffraction (XRD) profile [4], while the structure of $BaCu_2Ge_2O_7$ has not yet been reported. Very recently, Tsukada et al. prepared a single crystal of $BaCu_2Si_2O_7$ and reported its susceptibility and neutron scattering data [5]. We have prepared polycrystalline samples of these two compounds as well as their solid solutions and studied their structural and magnetic properties in detail. As a result, it is evidenced that they represent an outstanding 1D HAF system with linearly adjustable interactions between $J=$ 290 K ($x=0$) and 580 K ($x=1$). This change must probably be correlated with the small change in the Cu–O–Cu bond angle from 121° ($x=0$) to 128° ($x=1$).

2. Experimental

Polycrystalline samples of $BaCu_2Si_2O_7$, $BaCu_2Ge_2O_7$, and $BaCu_2(Si_{1-x}Ge_x)_2O_7$ ($x=0.025$, 0.05, 0.075, 0.1, 0.15, 0.25, 0.5, 0.75, 0.9, 0.95) were prepared by a standard solid state reaction method as follows. An appropriate mixture of $BaCO_3$ (3N), SiO_2 (3N), GeO_2 (3N), and CuO (4N) powders was ground in an agate mortar,

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pressed into a pellet, and calcined at 850°C in air for 12 h. Then the product was treated several times in the same manner at higher temperatures up to 1015°C for 50 h in total with intermittent grinding and pelletization. After the final heat treatment the product was quenched to room temperature in air. Thus obtained samples showed blue color; bright blue for the Si side, and dark blue for the Ge side. All the samples were electrical insulators.

The samples were investigated by means of powder XRD with graphite-monochromated Cu Kα radiation. The crystal structure was refined by means of a Rietveld analysis of the powder XRD patterns using the software RIETAN [6]. Data for this were collected at room temperature over a 2θ range 10–120° at a 0.02° step for 10 s. The magnetic susceptibility was measured on a Quantum Design SQUID magnetometer (MPMS-XL) typically in an applied field of 0.1 T from 2 to 400 K. The specific heat was measured between 2 and 30 K by a relaxation method in a Quantum Design Physical-Property-Measurement-System (PPMS).

3. Results and discussion

The reported structural analysis on $BaCu_2Si_2O_7$ gave an orthorhombic space group of *Pnma* with lattice dimensions of $a=6.866$, $b=13.190$ and $c=6.906$ Å [4]. Starting from the atomic coordinates given there, we carried out Rietveld analyses for both the Si- and Ge-phases. Fig. 1 illustrates the results, showing an excellent fit between observed and calculated patterns in each case. The resulting structural parameters and their estimated standard deviations are listed in Tables 1 and 2. The lattice constants are $a=6.86058(8)$, $b=13.17507(17)$ and $c=6.89589(8)$ Å for the Si compound, and $a=7.04765(6)$, $b=13.40700(9)$ and $c=7.02755(5)$ Å for the Ge compound. R factors are $R_{wp}=1.65\%$, $R_e=2.63\%$, $R_p=1.24\%$, $R_B=4.04\%$, and $R_F=3.66\%$ for the Si compound, and $R_{wp}=1.58\%$, $R_e=2.80\%$, $R_p=1.11\%$, $R_B=2.27\%$, and $R_F=1.40\%$ for the Ge compound. The goodness-of-fit index, R_{wp}/R_e, is 0.63 and 0.57, respectively. The obtained structural parameters for $BaCu_2Si_2O_7$ are in good agreement with the previous report. The small R factors for $BaCu_2Ge_2O_7$ confirmed that the Ge analogue is isostructural with the Si compound.

The crystal structure is illustrated schematically in Fig. 2. The key units are obviously the CuO_4 squares (or flattened CuO_4 tetrahedra) and $(Si,Ge)_2O_7$ groups made of a pair of corner-shared $(Si,Ge)O_4$ tetrahedra. The CuO_4 squares are connected to each other by their corners and form 1D chains along the c axis. Note that they are heavily corrugated to an intrachain Cu–O–Cu bond angle θ of 121.0° for Si and 128.4° for Ge. In the previous studies on a series of compounds with edge-sharing CuO_2 chains [3], it was pointed out that the superexchange coupling changes

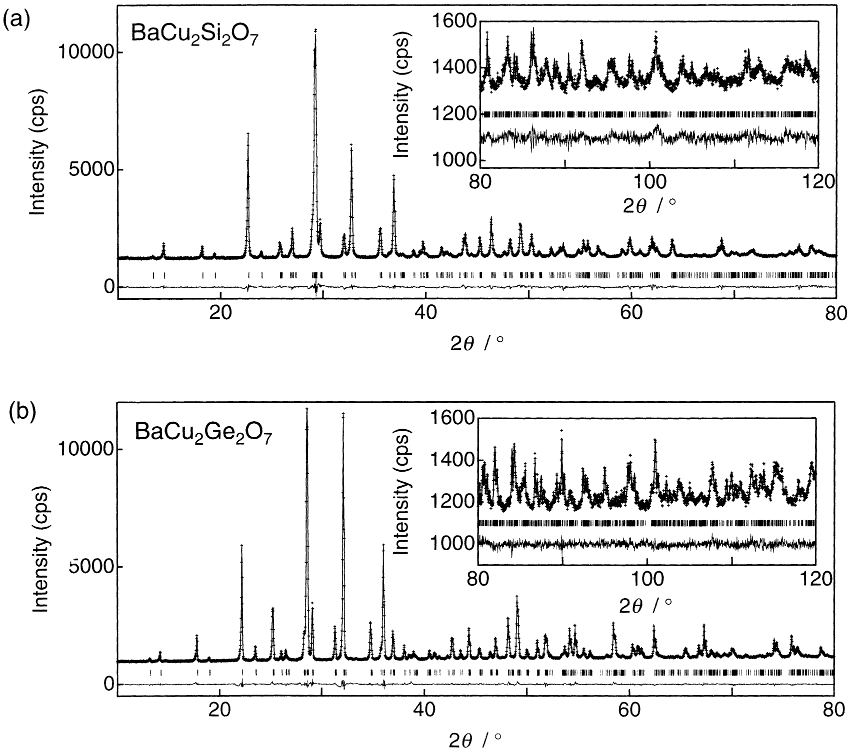

Fig. 1. Rietveld-refinement patterns for (a) $BaCu_2Si_2O_7$ and (b) $BaCu_2Ge_2O_7$. Observed diffraction intensities are represented by plus (+) marks, and the calculated patterns by the solid lines. Differences between the observed and calculated intensities are given near the bottom. Short vertical marks indicate the position of allowed Bragg reflections.

Table 1
Fractional atomic coordinates and atomic displacement parameters for $BaCu_2Si_2O_7$[a]

Atom	Wyckoff position	x	y	z	B_{iso} (Å^2)
Ba	4*c*	−0.0115(3)	0.25	0.9558(2)	1.77(4)
Cu	8*d*	0.2214(3)	0.0052(2)	0.7927(3)	1.80(6)
Si	8*d*	0.0045(9)	0.1337(2)	0.4732(6)	0.66(8)
O1	4*c*	0.0775(13)	0.25	0.4781(14)	−0.01(30)
O2	8*d*	−0.1617(13)	0.1311(8)	0.6238(12)	1.97(25)
O3	8*d*	−0.0698(13)	0.1155(8)	0.2619(10)	2.33(30)
O4	8*d*	0.1809(9)	0.0649(5)	0.5299(12)	0.58(22)

[a] Space group *Pnma*; $a=6.86058(8)$ Å, $b=13.17507(17)$ Å, $c=6.89589(8)$ Å; $Z=4$.

Table 2
Fractional atomic coordinates and atomic displacement parameters for $BaCu_2Ge_2O_7$[a]

Atom	Wyckoff position	x	y	z	B_{iso} (Å^2)
Ba	4*c*	−0.0210(2)	0.25	0.9485(1)	0.59(3)
Cu	8*d*	0.2172(3)	0.0040(2)	0.7980(3)	0.63(4)
Ge	8*d*	−0.0077(3)	0.1305(1)	0.4710(3)	0.19(3)
O1	4*c*	0.1007(11)	0.25	0.4831(13)	0.08(27)
O2	8*d*	−0.1884(9)	0.1364(6)	0.6341(9)	0.99(21)
O3	8*d*	−0.0563(10)	0.1143(6)	0.2357(8)	0.94(22)
O4	8*d*	0.1696(8)	0.0476(5)	0.5365(12)	0.49(20)

[a] Space group *Pnma*; $a=7.04765(6)$ Å, $b=13.40700(9)$ Å, $c=7.02755(5)$ Å; $Z=4$.

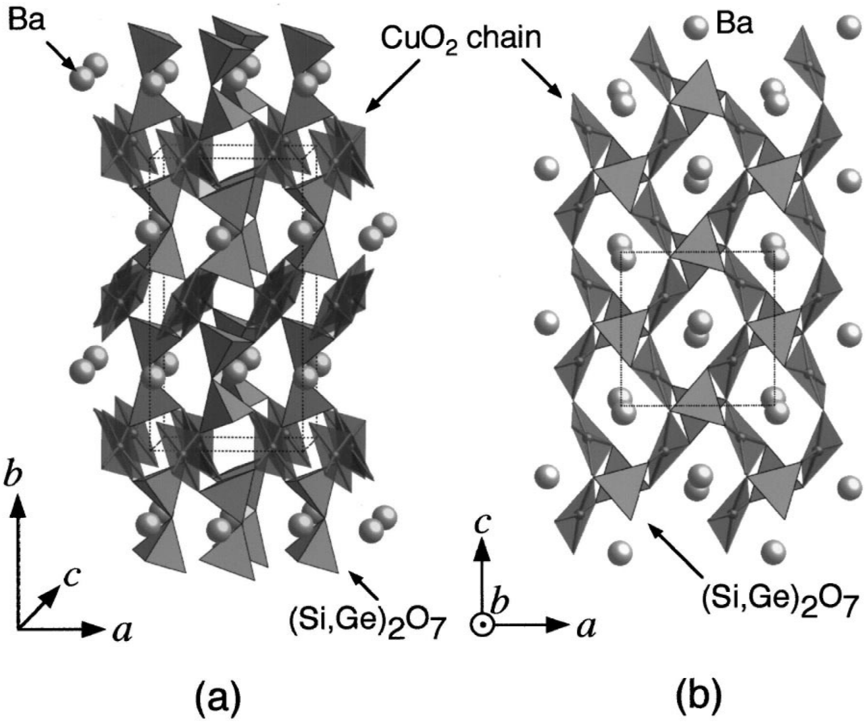

Fig. 2. Schematic representation of the crystal structure for $BaCu_2(Si_{1-x}Ge_x)_2O_7$ perspectively viewed along the c axis (a) and along the b axis (b). Corner-sharing, corrugated CuO_3 chains exist along the c axis with $(Si,Ge)_2O_7$ groups and Ba ions intervening. Significant interchain magnetic interactions are expected along the a axis.

their sign depending upon the Cu–O–Cu bond angle from F ($\theta \leq 95°$) to AF ($\theta \geq 95°$). Then, it is expected that the chains with $\theta = 120$–$130°$ in the present compounds possess rather large AF couplings, though they must be significantly smaller than 2200 K for the linear chains in $SrCuO_2$. Concerning interchain couplings which must be much smaller than intrachain couplings, it is likely that those along the *b* axis over a distance of 6.5 Å would be much weaker than those along the *a* axis.

Fig. 3 shows the temperature dependence of magnetic susceptibility χ for the two compounds measured in an applied field of 0.1 T. Each set of data exhibits a broad, rounded maximum, indicating short-range AF correlations characteristic of low-dimensional HAF systems. However, the temperature of the maximum is quite different; 170 K for Si and 360 K for Ge. In addition the magnitude of χ is much reduced in $BaCu_2Ge_2O_7$. These facts imply that the intrachain interaction *J* is much larger in $BaCu_2Ge_2O_7$. The behavior at low temperature below the maximum is also quite different: the χ of $BaCu_2Si_2O_7$ shows a slight upturn and then drops suddenly around 10 K, while in $BaCu_2Ge_2O_7$ a similar upturn is followed by a steep increase below 10 K and finally by a saturation as shown in the inset to Fig. 3.

The broad maximum at high temperature could be reproduced by assuming that

$$\chi = \chi_0 + \chi_{CW} + \chi_{BF},$$

where χ_0 is a temperature-independent term coming from the core diamagnetism and the Van Vleck paramagnetism, and χ_{CW} is a Curie–Weiss contribution ($\chi_{CW} = C/(T - \Theta)$), the origin of which will be discussed later. χ_{BF} is the susceptibility for $S = 1/2$ HAF chains calculated numerically by Bonner and Fisher [7]. The following parameterized function was used to fit the data

$$\chi_{BF} = (Ng^2\mu_B{}^2/(k_BT))(A + By^{-1} + Cy^{-2})/$$
$$(1 + Dy^{-1} + Ey^{-2} + Fy^{-3}),$$

where $A = 0.250654$, $B = 0.0398637$, $C = 0.025211$, $D = 0.361143$, $E = 0.224491$, and $F = 0.142647$. $y = k_BT/J$, *g* is the *g*-factor, μ_B is the Bohr magneton, and k_B is the Boltzmann constant. The *g*-factor was fixed to 2.1 in every case which is a typical value for cupric oxides. Fitting was done at $T > 30$ (20) K for the Si (Ge) compound.

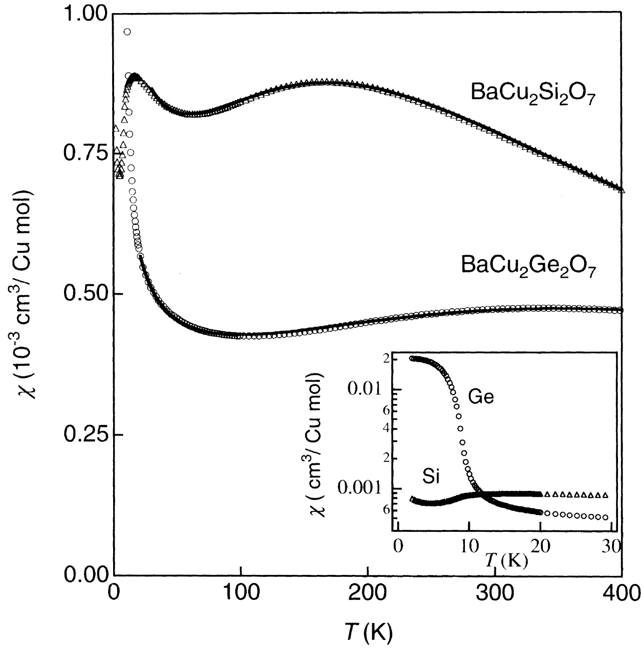

Fig. 3. Temperature dependence of magnetic susceptibility χ for $BaCu_2Si_2O_7$ and $BaCu_2Ge_2O_7$, which was measured with increasing temperature from 2 to 400 K in a magnetic field of 0.1 T. The solid line on each data set is a fit to the model described in the text. The inset shows a semi-logarithmic plot of the same data at low temperature.

The AF coupling *J* was determined to be 291 (578) K for the Si (Ge) compound; a factor of two larger for $BaCu_2Ge_2O_7$. The value for $BaCu_2Si_2O_7$ compound is in good agreement with that estimated from neutron scattering experiments ($J = 289$ K). This tendency is actually consistent with the above discussion on the relation between *J* and the Cu–O–Cu bond angle ($\theta = 121°$ (Si) and 128° (Ge)). It would be remarkable if such a small change in θ gives rise to the observed large difference in *J*. It is noted, however, that *J* is also very sensitive to θ around 90°; -100 K ($\theta \sim 94°$) and 140 K for $CuGeO_3$ ($\theta = 99°$). An additional factor to be possibly taken into account is the superexchange interaction through $Si(Ge)O_4$ tetrahedra to which the 2p (Si) and the 3p orbitals (Ge) would contribute. It is proposed that in $CuGeO_3$ the 3p orbitals of Ge^{4+} are mixed with oxygen 2p orbitals and thus play a crucial role in the superexchange interactions between Cu^{2+} spins. The 2p orbitals of Si^{4+} may not contribute so much because of their depth.

In order to get more insight into the magnetic phase transitions, we have measured the specific heat *C* which is usually more sensitive to a phase transition than the magnetic susceptibility. The results are shown in Fig. 4, where C/T is plotted against *T*. A small but distinct peak in C/T is seen around 9 K in each compound, which exactly corresponds to the inflection point of the χ–T curve. Consequently the peak in C/T indicates the occurrence of magnetic order, and the critical temperature T_N was determined from the peak-top temperature to be 8.9 and 8.6 K for the Si and Ge compound, respectively.

The peak in specific heat is considerably small and broad, suggesting that the transition is of the second order. This may exclude the possibility of any structural transition accompanying the magnetic transition. The small peak as well as low T_N imply that most of the magnetic entropy is lost due to the short-range ordering above T_N and below J/k_B, as generally seen in low-dimensional antiferromagnets. The smaller peak in the Ge compound should reflect its larger *J* value. Though quantitative discussion on the magnetic entropy was not possible because it was difficult

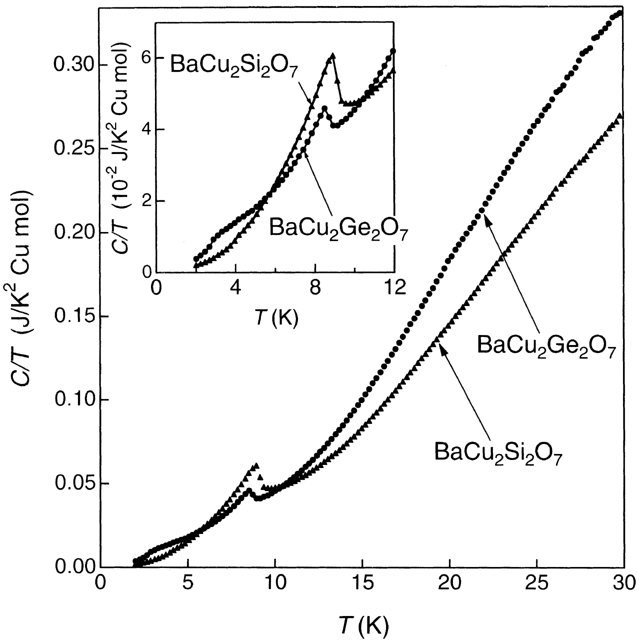

Fig. 4. Temperature dependence of specific heat C. C/T is plotted against T.

to extract the lattice contribution precisely from the raw data, these specific heat data may be considered to be consistent with the picture that the present compounds are excellent quasi-1D systems with $k_B T_N / J = 1.5$–3.0%.

We have prepared solid solutions $BaCu_2(Si_{1-x}Ge_x)_2O_7$ with $x = 0.025$, 0.05, 0.075, 0.1, 0.15, 0.25, 0.5, 0.75, 0.9, 0.95 and found that there is no miscibility gap between the parent compounds. The lattice parameters determined by the Rietveld refinement change linearly with x as expected from the Vagard's law (Fig. 5). The ionic radius of a tetrahedrally coordinated Si^{4+} ion is 0.26 and that of a Ge^{4+} ion is 0.39. The observed lattice expansion with increasing x can be ascribed to this ionic size difference. We should note that the c axis, which is the chain axis, expands with x as the other axes. This seems to be against the general tendency that a substituted 1D chain compound expands or contracts little along the direction of chains. This tendency applies, however, to linear chains. In the present compounds, the expansion of the c axis results from the change in the bond angle θ, not from the change in Cu–O bond length. And it is the tunability of θ that leads to the adjustable J.

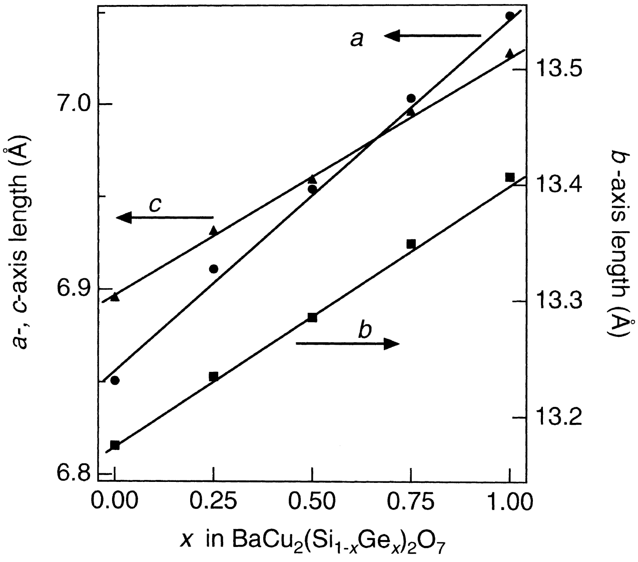

Fig. 5. Composition dependence of lattice parameters for $BaCu_2(Si_{1-x}Ge_x)_2O_7$.

The magnetic susceptibility of the solid solution changes continuously with composition as shown in Fig. 6: the position of the broad maximum systematically shifts to higher temperature and the height becomes lower with increasing x. To evaluate J, fitting of χ was done as for the parent compounds. The results are summarized in the inset to Fig. 7. The J parameter has been found to increase almost linearly with x. Fig. 7 shows the magnetic susceptibility for all the samples normalized by the J parameter. It exhibits an obvious universal behavior particularly at high temperatures, tracing the Bonner–Fisher curve where the peak maximum should appear at $\chi J / N g^2 \mu_B^2 \sim 0.1469$ and $k_B T / J \sim 0.641$ [7]. The non-universal behavior observed below the maximum is due to additional Curie-like contributions which depend on the composition.

The anomalies observed at low temperature are probably due to the development of magnetic LRO. In general, quasi-1D compounds exhibit LRO at low temperature owing to small interchain interactions. In the case of

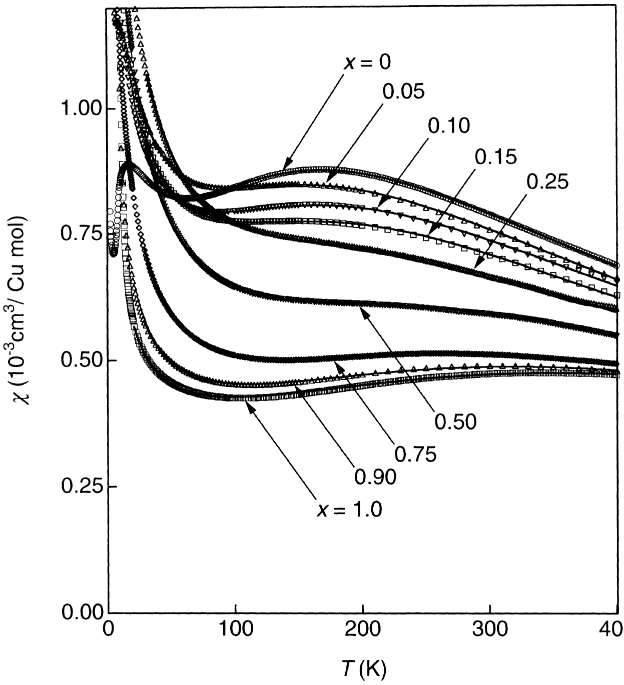

Fig. 6. Magnetic susceptibility for the solid solution $BaCu_2(Si_{1-x}Ge_x)_2O_7$. A solid line on each set of data points is a fit to the model described in the text.

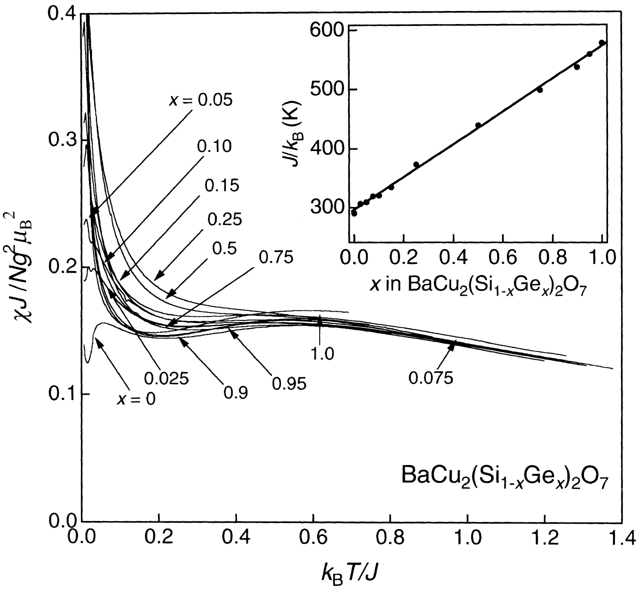

Fig. 7. Universal behavior seen in the $\chi(T)$ curves normalized by the intrachain interaction J parameter. The inset shows the composition dependence of J showing a linear variation with x.

Sr_2CuO_3 LRO occurs at $T_N = 5.4$ K; $k_B T_N / J \sim 0.25\%$. It is remarkable that the two isostructural compounds with nearly the same T_N exhibit different types of magnetic order in such a way that a weak ferromagnetic moment is observed only for the Ge compound. The weak ferromagnetic moment is estimated to be 6.5×10^{-3} μ_B/Cu. Since the inversion center between adjacent Cu^{2+} ions is missing in the crystal structure, the Dzyaloshinsky–Moriya interaction [8] is expected to occur leading to an uncompensated moment due to a slight tilting of adjacent spins. That is, the weak ferromagnetism of $BaCu_2Ge_2O_7$ is due to canted antiferromagnetism. In contrast, $BaCu_2Si_2O_7$ seems to exhibit an ordinary AF order without net moments. This striking difference in the magnetic order between the two isostructural crystals is very interesting and should be explained reasonably, which will be described elsewhere.

Concerning the χ, we have always observed Curie-like divergence below the broad maximum. It is reasonable to assume that this comes from the net moments of chains. Because the intrachain interaction is very large, and thus AF correlations are well developed even at high temperatures, one can consider approximately the system as composed of small net moments of weakly interacting chains. The Curie constants deduced from fitting the χ data correspond to paramagnetic moments of 0.3–0.5 μ_B.

4. Conclusions

We have shown that $BaCu_2(Si_{1-x}Ge_x)_2O_7$ represents a unique class of the $S = 1/2$ 1D HAF system with tunable intrachain couplings between 290 and 580 K depending on the Si/Ge composition. This feature originates from the corrugated and slightly retractable structure of the corner-sharing CuO_3 chains.

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