Magnetic excitations from the linear Heisenberg antiferromagnetic spin trimer system $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb)

M. Matsuda and K. Kakurai
Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan

A. A. Belik,* M. Azuma, and M. Takano
Institute for Chemical Research, Kyoto University, Gokasho, Uji 610-0011, Japan

M. Fujita
Institute for Materials Research, Tohoku University, Katahira, Sendai 980-8577, Japan
(Received 24 May 2004; revised manuscript received 5 October 2004; published 19 April 2005)

Inelastic neutron-scattering experiments were performed on $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb), which consists of one-dimensional array of linear copper spin trimers. It was found that the magnetic excitations are well described by the linear Heisenberg antiferromagnetic spin trimer model, in which the main interaction is the nearest-neighbor intratrimer interaction and the weak next-nearest-neighbor intratrimer and intertrimer interactions are expected. The intratrimer coupling constants are determined to be 9.45(3), 10.04(3), and 9.13(2) meV for $A_3Cu_3(PO_4)_4$ with A=Ca, Sr, and Pb, respectively. The other interactions were found to be very small.

DOI: 10.1103/PhysRevB.71.144411 PACS number(s): 75.10.Jm, 75.25.+z

I. INTRODUCTION

Recently, molecular clusters composed by a large number of magnetic ions have attracted much interest since they are an ideal model system of nanometer-sized single-domain magnetic particles with high spin ground state.[1] Some of the systems exhibit fascinating quantum properties such as quantum tunneling in the magnetization. On the other hand, the magnetic cluster system with a small number of spins with spin (S) $\frac{1}{2}$ is also considered to be interesting since the quantum effect is much enhanced. In the $S=\frac{1}{2}$ one-dimensional (1D) alternating Heisenberg antiferromagnets the ground state is a singlet state, in which singlet dimers are coupled one dimensionally. The alternating interactions are sometimes caused by the spin-Peierls transition, in which the spin-lattice coupling is important. Another interesting example is the antiferromagnetic spin trimer system. $La_4Cu_3Mo_3O_{12}$ is a model system for the triangle $S=\frac{1}{2}$ spin trimer system, weakly coupled quasi-two-dimensionally. Magnetic susceptibility and neutron-scattering studies showed that the compound is well described by the isolated Heisenberg triangle spin trimer model,[2,3] in which the antiferromagnetic intratrimer interactions are frustrated. As a result, the zero-temperature magnetic structure is very sensitive to the intra trimer and intertrimer interactions.[3]

$A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb) is another candidate for studying the spin trimer antiferromagnetism.[4–7] There are two Cu sites in the compounds. The Cu(1) is surrounded by four oxygens forming a square plane. The Cu(2) is surrounded by five oxygens forming a distorted square pyramid. A schematic view of the structure and the magnetic interactions in the copper chains is shown in Fig. 1.[8] The exchange interaction sensitively depends on the bond angle and bond length between the Cu spins. Consideration of the crystal structure and the Goodenough rules[9,10] indicate that the absolute value of the nearest-neighbor intratrimer interaction $J_1(>0)$ is much stronger than that of the next-nearest-neighbor intratrimer interaction J_1' and the intertrimer interaction J_2. Therefore, these compounds are considered to be a model system for the antiferromagnetic $S=\frac{1}{2}$ spin trimer in a

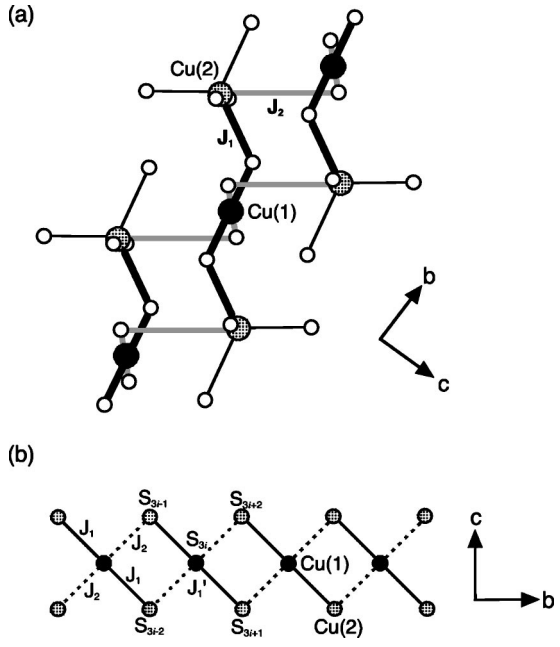

FIG. 1. (a) Projection of the exchange pathways in $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb). The large and filled circles represent the Cu^{2+} moments. The small and open circles represent the oxygen ions. The black and gray circles represent the Cu(1) and Cu(2), respectively. The thick black and gray lines show the pathways of J_1 and J_2, respectively. (b) Schematic view of the major magnetic interactions J_1, J_1', and J_2 in the one-dimensional array of copper spin trimers. J_1' is the next-nearest-neighbor interaction between edge spins in the trimer.

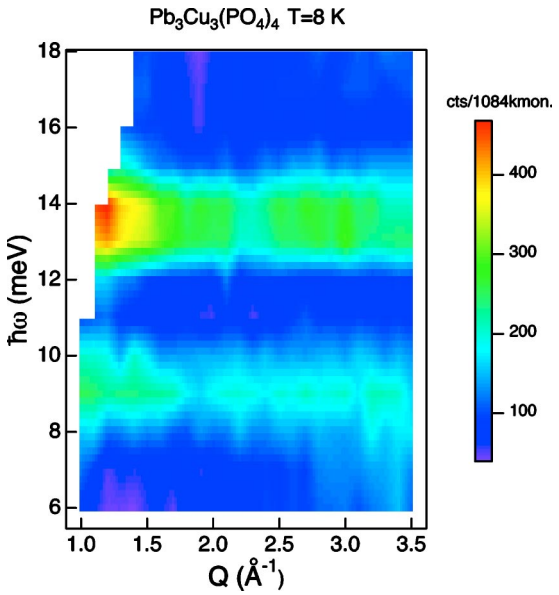

FIG. 2. (Color online) Image plot of the neutron-scattering intensity in $\hbar\omega - Q$ space at 8 K in $Pb_3Cu_3(PO_4)_4$.

line. The model Hamiltonian with Heisenberg exchange interactions is described as

$$H = J_1 \sum \boldsymbol{S}_{3i}(\boldsymbol{S}_{3i-1} + \boldsymbol{S}_{3i+1}) + J_1' \sum \boldsymbol{S}_{3i-1}\boldsymbol{S}_{3i+1} + J_2 \sum \boldsymbol{S}_{3i}(\boldsymbol{S}_{3i-2} + \boldsymbol{S}_{3i+2}). \quad (1)$$

Since the intratrimer interactions are not frustrated in this system, it is rather straightforward to compare the experimental results with the theoretical ones in order to understand the trimer antiferromagnetism.

The magnetic susceptibility and heat-capacity measurements on $A_3Cu_3(PO_4)_4$ with A=Ca and Sr show that the intratrimer interaction $J_1(\sim 100$ K) is much larger than the intertrimer interaction $J_2(\sim 3$ K).[11] Magnetization measurements show that there exists a plateau with a saturated value of $1.15\mu_B$.[11,12] The magnetic susceptibility measurements also show a signature of 1D ferrimagnets at low temperatures.[5,11] A long-range magnetic ordering was reported in $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb) from the magnetic susceptibility and heat-capacity measurements.[5,13] The transition temperatures are 0.9, 0.9, and 1.3 K for $A_3Cu_3(PO_4)_4$ with A=Ca, Sr, and Pb, respectively. These temperatures are extremely low compared to the fairly large J_1. All these results suggest that these compounds are the ideal model antiferromagnetic spin trimer systems, in which intertrimer interaction is small, and the ground state is a state with $S=\frac{1}{2}$.

In the isolated Heisenberg antiferromagnetic $S=\frac{1}{2}$ trimer in a line the energy-level scheme is described as follows. The ground state is a doublet with $E(0)=-J_1$ and $S_T=\frac{1}{2}$, where J_1 is the intratrimer interaction and S_T is the total spin of a trimer. The first and second excited states are a doublet with $E(1)=0$ and $S_T=\frac{1}{2}$ and a quartet with $E(2)=\frac{1}{2}J_1$ and $S_T=\frac{3}{2}$, respectively. When the Ising- or XY-like anisotropy is pronounced, the quartet is split into two doublets, whereas the two doublets remain degenerate. In the extreme cases of the Ising and XY systems, the first and second excited states are a quartet and a doublet, respectively.

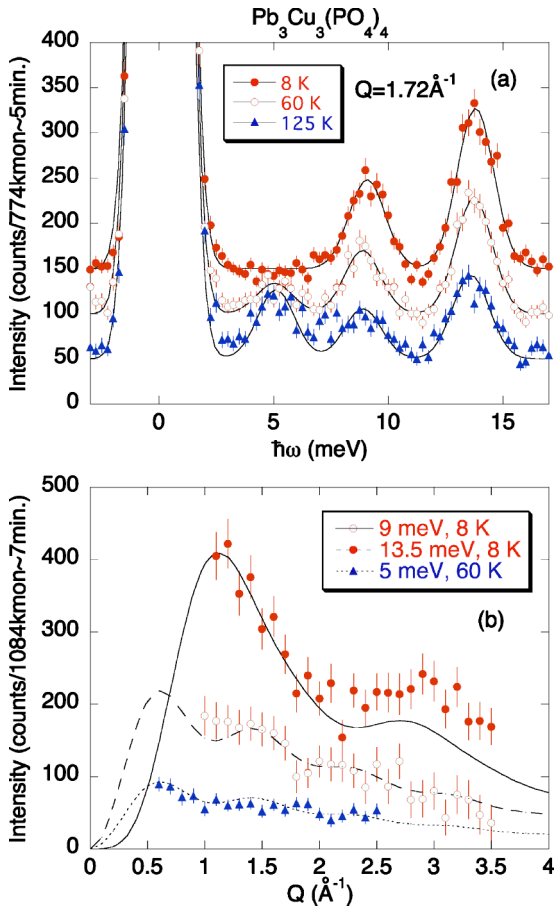

FIG. 3. (Color online) (a) Constant-Q scans at various temperatures in $Pb_3Cu_3(PO_4)_4$. The solid lines are the results of fits with Gaussians. Fifty counts are added at each successive temperature so that the scans are compared on one graph. The elastic-scattering intensity originates from both the nuclear incoherent scattering and paramagnetic scattering. (b) Q dependence of neutron-scattering intensity at $\hbar\omega$=5 meV at T=60 K and at $\hbar\omega$=9 meV and 13.5 meV at T=8 K. For the data at T=8 K, background intensity measured at a different energy, at which the magnetic signal is almost negligible, is subtracted from the raw data. For the data at T=60 K, background intensity measured at T=8 K is subtracted from the raw data. The lines show the intensity calculated with Eq. (3).

The neutron-scattering technique is an ideal tool to directly investigate the energy-level scheme of the spin trimer system as mentioned above. We have performed inelastic neutron-scattering experiments on the polycrystalline samples of $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb). Since a cluster of the linear spin trimer is well isolated, almost dispersionless and sharp excitation peaks are observed even in the powder measurements. Our analysis of the temperature and Q dependencies on the scattering intensities indicates that these compounds are well described by the isolated Heisenberg antiferromagnetic spin trimer model.

II. EXPERIMENTAL DETAILS

The polycrystalline samples of $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb) were synthesized by the conventional solid-state reaction at 1183, 1183, and 998 K, respectively. About 10 g of the sample was used in the measurements. Detail of the sample characterization is described elsewhere.[6,7,13]

The inelastic neutron-scattering experiments were carried out on the thermal neutron three-axis spectrometer TAS2 installed at the guide hall of JRR-3 at Japan Atomic Energy Research Institute. The fixed final neutron energy was 13.7 meV. Contamination from higher-order beams was effectively eliminated using pyrolytic graphite filters. The horizontal collimator sequences were guide-80′-S-80′-open. The samples were mounted in a closed cycle refrigerator. The measurements were performed well above the transition temperatures, where the spin trimer magnetism is distinct.

III. THEORETICAL BACKGROUND

A detailed formulation for the neutron cross section in the magnetic cluster system was performed by Furrer and Güdel.[14] Experimentally, the excitations from the trimers as well as dimers and tetramers were observed in $CsMn_xMg_{1-x}Br_3$, in which quasi-one-dimensional Mn^{2+} ions $\left(S=\frac{5}{2}\right)$ are diluted by the nonmagnetic Mg^{2+} ions.[15] It was confirmed that the excitations can be well described by the calculation.

For the isolated antiferromagnetic trimer in a line, the quantum numbers to describe the spin state are the total spin quantum number $\boldsymbol{S}=\boldsymbol{S_1}+\boldsymbol{S_2}+\boldsymbol{S_3}$ and the additional quantum number $\boldsymbol{S_{13}}=\boldsymbol{S_1}+\boldsymbol{S_3}$. For $S_1=S_2=S_3$ the eigenvalues of the Hamiltonian (1) with $J_2=0$ are

$$E(S_{13},S)=\frac{J_1}{2}[S(S+1)-S_{13}(S_{13}+1)-S_1(S_1+1)] + \frac{J_1'}{2}[S_{13}(S_{13}+1)-2S_1(S_1+1)], \quad (2)$$

with $0\leqslant S_{13}\leqslant 2S_1$ and $|S_{13}-S_1|\leqslant S\leqslant S_{13}+S_1$. For the isolated antiferromagnetic trimer in a line with $S=\frac{1}{2}$, the ground state is a doublet with $|S_{13}=1,S=\frac{1}{2}\rangle\left(E(0)=-J_1+\frac{1}{4}J_1'\right)$. The first and second excited states are a doublet with $|0,\frac{1}{2}\rangle\left(E(1)=-\frac{3}{4}J_1'\right)$ and a quartet with $|1,\frac{3}{2}\rangle\left(E(2)=\frac{1}{2}J_1+\frac{1}{4}J_1'\right)$, respectively.

The neutron-scattering cross sections for a powder sample for a transition $|S_{13},S\rangle\rightarrow|S_{13}',S'\rangle$ are described as follows:

$$I_{|1,1/2\rangle\rightarrow|0,1/2\rangle}\propto 3C_0\rho(0)\left[1-\frac{\sin(2QR)}{2QR}\right]\times\delta[\hbar\omega+E(0)-E(1)],$$

$$I_{|1,1/2\rangle\rightarrow|1,3/2\rangle}\propto 2C_0\rho(0)\left[3+\frac{\sin(2QR)}{2QR}-4\,\frac{\sin(QR)}{QR}\right]\times\delta[\hbar\omega+E(0)-E(2)],$$

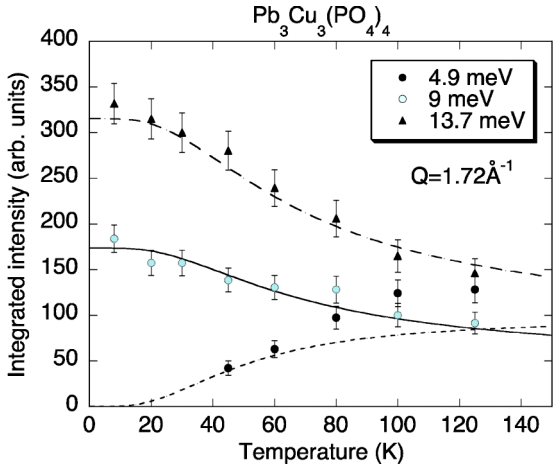

FIG. 4. Temperature dependence of the integrated intensities at 4.9, 9, and 13.7 meV in $Pb_3Cu_3(PO_4)_4$. The lines are calculated using Eq. (3).

$$I_{|0,1/2\rangle\rightarrow|1,3/2\rangle}\propto 6C_0\rho(1)\left[1-\frac{\sin(2QR)}{2QR}\right]\times\delta[\hbar\omega+E(1)-E(2)], \quad (3)$$

where

$$C_0=\frac{k'}{k}F^2(Q)\exp[-2W(Q)],$$

$$\rho(n)=Z^{-1}\exp\left[-\frac{E(n)}{k_BT}\right].$$

k and k' are the wave numbers of incident and final neutrons, respectively. $F(Q)$, $\exp[-2W(Q)]$, and Z are the magnetic form factor, the Debye-Waller factor, and the partition function, respectively. The magnetic excitations are expected at $E(1)-E(0)=J_1-J_1'$, $E(2)-E(0)=\frac{3}{2}J_1$, and $E(2)-E(1)=\frac{1}{2}J_1+J_1'$.

When the intertrimer interaction J_2 becomes nonnegligible, each excited state should become dispersive. In powder measurements, this effect broadens the excitation width in energy.

IV. RESULTS AND DISCUSSION

Figure 2 shows an image plot of the inelastic neutron-scattering spectra measured at 8 K in $Pb_3Cu_3(PO_4)_4$. There are two flat excitations at $\hbar\omega\sim 9$ meV and $\sim$13.5 meV. The sharp dispersionless excitations indicate that J_2 is small as described in Sec. III. A characteristic modulation of the intensity as a function of Q is also recognized.

Temperature dependence of the inelastic neutron spectra in constant-Q scans in $Pb_3Cu_3(PO_4)_4$ is shown in Fig. 3(a). The positions of the excitation peaks at 8 K are shown in Table I. It was confirmed that the energy positions are almost independent of temperature. The intensity at 13.69 meV is about a factor of $\sim$2 larger than that at 9.00 meV. With increasing temperature intensities at 9.00 meV and 13.69

TABLE I. The magnetic excitation energies and the intratrimer coupling constants at 8 K in $A_3Cu_3(PO_4)_4$ (A=Pb, Ca, and Sr).

A	$E(1)-E(0)$ (meV)	$E(2)-E(0)$ (meV)	J_1 (meV)	J_1' (meV)
Pb	9.00(5)	13.69(3)	9.13(2)	0.13(7)
Ca	9.33(5)	14.17(4)	9.45(3)	0.12(8)
Sr	9.93(6)	15.06(4)	10.04(3)	0.11(9)

meV decrease, whereas a new excitation peak develops at 4.9 meV. Figure 3(b) shows the Q dependence of the peak intensities of these excitations at $\hbar\omega$=5 meV at T=60 K and at $\hbar\omega$=9 meV and 13.5 meV at T=8 K. The solid lines in Fig. 3(a) are the results of fits with Gaussians. In the fittings the widths of the three excitations are fixed at the same value to minimize the number of fitting parameters. The energy resolution is calculated to be 1.7 and 2.3 meV full width at half maximum at $\hbar\omega$=5 and 14 meV, respectively. The excitation width at 8 K is fitted to be 1.87(5) meV, which is close to the averaged values of the energy resolution at $\hbar\omega$=5 and 14 meV. This indicates that the excitations are almost resolution limited and almost dispersionless. It is noted that the width is almost temperature independent.

The temperature dependence of the integrated intensities of the 4.9, 9, and 13.7 meV excitation peaks at Q =1.72 Å^{-1} is plotted in Fig. 4. The lines are the results of the calculation with the cross sections, Eq. (3). We assumed that $W(Q)$=0. It is noted that the only variable parameter is the overall scale factor. Other parameters are fixed. R is fixed at 3.6 Å, which corresponds to the averaged distance between two neighboring copper spins in the trimer. The calculation describes the observed intensities reasonably well. The only discrepancy is that the observed intensity at 4.9 meV becomes larger than the calculated values above ~80 K. One possibility is that phonon contribution becomes nonnegligible at higher temperatures around 5 meV. The Q dependence of the intensities shown in Fig. 3(b) is also described by Eq. (3) using the same parameters. The calculation describes the observed intensities reasonably well although the observed value is slightly larger at higher Q around 3 Å^{-1}. It is also probable that the scattering from phonons is superimposed. The very low-Q data, where the magnetic scattering is expected to increase with increasing

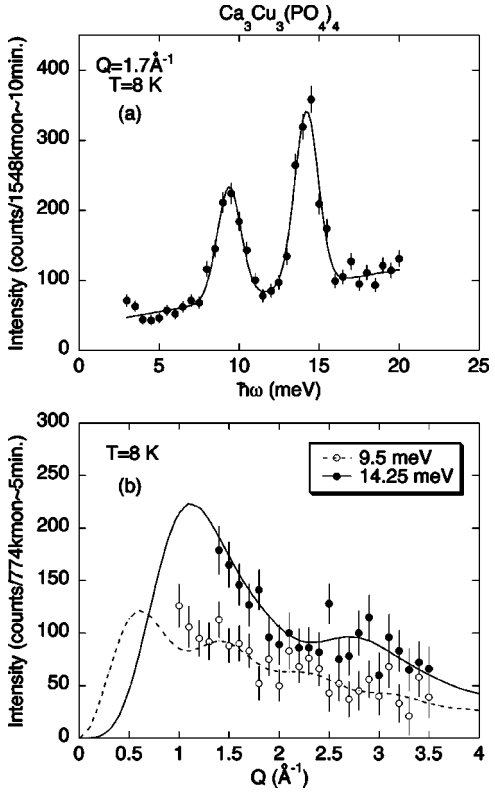

FIG. 5. (a) Constant-Q scans at 8 K in $Ca_3Cu_3(PO_4)_4$. The solid line is the result of a fit with two Gaussians. (b) Q dependence of neutron-scattering intensity at 9.5 meV and 14.25 meV. Background intensity measured at a different energy is subtracted from the raw data. The lines show the intensity calculated using Eq. (3).

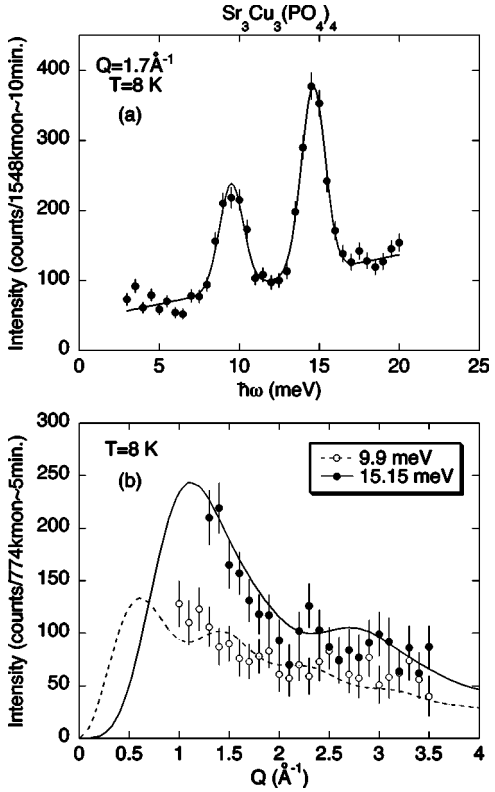

FIG. 6. (a) Constant-Q scans at 8 K in $Sr_3Cu_3(PO_4)_4$. The solid line is the result of a fit with two Gaussians. (b) Q dependence of neutron-scattering intensity at 9.9 meV and 15.15 meV. Background intensity measured at a different energy is subtracted from the raw data. The lines show the intensity calculated using Eq. (3).

Q, are missing because of the kinematical constraints. The lowest Q we could reach was 0.6 $Å^{-1}$ at 5 meV. The data show that the magnetic scattering decreases almost monotonically above 0.5 $Å^{-1}$, which is consistent with the calculation.

Figures 5 and 6 show the results of constant-Q and -ω scans in $Ca_3Cu_3(PO_4)_4$ and $Sr_3Cu_3(PO_4)_4$, respectively. The solid lines in Figs. 5(a) and 6(a) show the results of fits with two Gaussians. The positions of the excitation peaks are shown in Table I. The widths in energy are almost resolution-limited for both compounds. Therefore, the magnetic excitations are almost dispersionless as in $Pb_3Cu_3(PO_4)_4$. The lines in Figs. 5(b) and 6(b) show the results of fits with Eq. (3). The calculation describes the observed intensities reasonably well. The consistency for higher-Q data around 3 $Å^{-1}$ is better in these compounds than that in $Pb_3Cu_3(PO_4)_4$, suggesting that the phonon density of states depends on the weight of A element in $A_3Cu_3(PO_4)_4$. An optical mode probably exists at 13.5 meV in $Pb_3Cu_3(PO_4)_4$ just accidentally.

J_1 and J_1' are determined from the values of $E(1)-E(0)\,(=J_1-J_1')$ and $E(2)-E(0)\left(=\frac{3}{2}J_1\right)$ as shown in Table I. Since the dispersion is very flat, it is expected that the intertrimer interaction J_2 is considered to be very small. J_2 can be roughly estimated from the results of the magnetization measurements.[12] It was observed that the magnetization saturates at one-third of the value in the fully aligned ferromagnetic state. The field, at which the magnetization saturates, was ~10 T and ~20 T for $Ca_3Cu_3(PO_4)_4$ and $Sr_3Cu_3(PO_4)_4$, respectively. These values roughly correspond to J_2 so that the J_2 is ~1 meV. This is in contrast to the neutron result that the excitation width in energy is close to the instrumental resolution. However, the low magnetic ordering temperatures of ~1 K in $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb) indicate that J_2 is the same order of 0.1 meV, which is consistent with the neutron result. Further study is required in order to clarify this puzzling feature.

Since the exchange interactions depend sensitively on the structural parameters, that is, the bond length and bond angle between the Cu spins, it is difficult to calculate J_1, J_1', and J_2 in the real compounds. The averaged distances between Cu-O bond in the trimer unit are 2.008 Å, 2.035 Å, and 2.030 Å for $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb), respectively. The angles of the Cu-O-Cu bond are 123.6°, 124.8°, and 124.1° for $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb), respectively. These values are not directly related with J_1 shown in Table I. We showed experimentally that J_1 and J_1' have approximately the same values and J_2 is very small in the three compounds. As we described above, all the properties in $A_3Cu_3(PO_4)_4$ (A=Ca, Sr, and Pb) are consistent with those expected from the Heisenberg antiferromagnetic spin trimer model. This result indicates that the anisotropy in the exchange interaction is considered to be very small in these compounds.

In conclusion, our neutron-scattering studies showed that $A_3Cu_3(PO_4)_4$ with A=Ca, Sr, and Pb is a model system of the linear Heisenberg antiferromagnetic $S=\frac{1}{2}$ trimer. The intra trimer coupling constants are determined to be 9.45(3), 10.04(3), and 9.13(2) meV for $A_3Cu_3(PO_4)_4$ with A=Ca, Sr, and Pb, respectively. The interaction between the edge spins in the trimer and the intertrimer interaction were found to be very small.

ACKNOWLEDGMENTS

We would like to thank H. Ohta for stimulating discussions and Y. Shimojo for technical assistance.

*International Center for Young Scientists, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan.

[1] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science **265**, 1054 (1994).

[2] M. Azuma, T. Odaka, M. Takano, D. A. Vander Griend, K. R. Poeppelmeier, Y. Narumi, K. Kindo, Y. Mizuno, and S. Maekawa, Phys. Rev. B **62**, R3588 (2000).

[3] Y. Qiu, C. Broholm, S. Ishiwata, M. Azuma, M. Takano, R. Bewley, and W. J. L. Buyres, cond-mat/0205018 (unpublished).

[4] J. B. Anderson, E. Kostiner, and F. A. Ruszala, J. Solid State Chem. **39**, 29 (1981).

[5] M. Drillon, E. Coronado, M. Belaiche, and R. L. Carlin, J. Appl. Phys. **63**, 3551 (1988).

[6] H. Effenberger, J. Solid State Chem. **142**, 6 (1999).

[7] A. A. Belik, A. P. Malakho, B. I. Lazoryak, and S. S. Khasanov, J. Solid State Chem. **163**, 121 (2002).

[8] The space groups for $A_3Cu_3(PO_4)_4$ with A=Ca, Sr, and Pb are $P2_1/a$, $P2_1/a$, and $A2/a$, respectively. However, the structures of the 1D array of copper spin trimers are similar.

[9] J. B. Goodenough, Prog. Solid State Chem. **5**, 145 (1972).

[10] Y. Mizuno, T. Tohyama, S. Maekawa, T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **57**, 5326 (1998).

[11] M. Drillon, M. Belaiche, P. Legoll, J. Aride, A. Boukhari, and A. Moqine, J. Magn. Magn. Mater. **128**, 83 (1993).

[12] Y. Ajiro, T. Asano, K. Nakaya, M. Mekata, K. Ohyama, Y. Yamaguchi, Y. Koike, Y. Morii, K. Kamishima, H. Aruga-Katori, and T. Goto, J. Phys. Soc. Jpn. **70**, Suppl. A, 186 (2001).

[13] A. A. Belik, A. Matsuo, M. Azuma, K. Kindo, and M. Takano, J. Solid State Chem., (to be published).

[14] A. Furrer and H. U. Güdel, J. Magn. Magn. Mater. **14**, 256 (1979).

[15] U. Falk, A. Furrer, N. Furer, H. U. Güdel, and J. K. Kjems, Phys. Rev. B **35**, 4893 (1987).