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Magnetic excitations in the $S = \frac{1}{2}$ quasi-one-dimensional magnet $Sr_{14-x}Ca_xCu_{24}O_{41}$

M. Matsuda and K. Katsumata

The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan

S. M. Shapiro and G. Shirane

Physics Department, Brookhaven National Laboratory, Upton, New York 11973

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Abstract

Neutron scattering experiments have been performed on $Sr_{14-x}Ca_xCu_{24}O_{41}$ (x=3 and 6), which consists of CuO_2 chains and Cu_2O_3 ladders, in order to study the effect of Ca substitution on the dimerized state in the chains. The Ca substitution broadens the excitation peak although the excitation energy is almost unchanged. The effects of Ca and Y substitution on the dimerized state are compared.

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I. INTRODUCTION

$Sr_{14}Cu_{24}O_{41}$ consists of both two-leg ladders of copper ions and simple CuO_2 chains [1,2] as shown in Figs. 1(a) and (b). The two-leg ladders show an excitation gap as expected theoretically [3] at ∼35 meV [4]. An important feature of this compound is that stoichiometric $Sr_{14}Cu_{24}O_{41}$ contains hole carriers. It has been reported that most of the holes are localized in the chain and some exist in the ladder. [5–7] When Sr^{2+} sites are substituted by Ca^{2+} ions, total number of holes in the sample is unchanged but the holes in the chain are transferred to the ladder [6,7] and the system shows an insulator-to-metal transition [5,8]. Superconductivity was observed in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$ below T_c=10K under a high pressure of 3 GPa. [9] NMR studies have shown that the excitation gap energy is suppressed with hole doping. [10–12]. These results suggest a close relation between magnetism and transport properties.

The CuO_2 chains show an interesting dimerized state [13]. Figure 1(a) shows the CuO_2 chains in $Sr_{14}Cu_{24}O_{41}$. The copper ions are coupled by almost 90° Cu-O-Cu bond along the c axis. Each chain is well isolated from each other along the a and b axes. As mentioned above, there are localized holes in the chain. It is expected that the holes are localized at oxygen [6] and the hole spin couples with the copper spins to form a Zhang-Rice singlet [14]. These nonmagnetic Cu sites play an important role to form a dimerized state in the chain in $Sr_{14}Cu_{24}O_{41}$. The dimer is formed between next-nearest-neighbor Cu^{2+} spins along the c axis. The exchange interaction (∼10 meV) is mediated via a nonmagnetic ZR singlet. [15–17] Recently, Matsuda *et al.* [18] showed that the dimerized state can be explained with a model as shown in Fig. 1(c), which is ascribed to a quasi-two-dimensional hole ordering.

We have studied the Ca substitution effect on the dimerized state. The dimerized state in the chain is most stable in pure $Sr_{14}Cu_{24}O_{41}$. This dimerized state depends radically on the number of holes. When Y is substituted for Sr, the number of holes is decreased and the number of Cu^{2+} spins is increased. It is reported that in $Sr_{14-x}Y_xCu_{24}O_{41}$ system the magnetic excitation peaks broaden with Y substitution. [15,19] As mentioned above, the Ca

substitution for Sr also reduces the number of holes in the chain. [5–7] Therefore, the Ca substitution is expected to affect the dimerized state in the chain. It is important to study the Ca substitution effect in the chain as well as that in the ladder to clarify the magnetic and transport properties.

In this paper, we report the results of neutron scattering experiments on $Sr_{14-x}Ca_xCu_{24}O_{41}$ (x=3 and 6). It was observed that the magnetic inelastic peaks in the chain become broad with Ca substitution as in the case of Y substituted system. However, the dimerized state in the chain becomes unstable with Ca substitution much more gradually than with Y substitution. An interesting feature is that the excitation energy does not change with Ca substitution although it is decreased with Y substitution.

II. EXPERIMENTAL DETAILS

The single crystals of $Sr_{14-x}Ca_xCu_{24}O_{41}$ (x=3 and 6) were grown using a traveling solvent floating zone (TSFZ) method at 3 bars oxygen atmosphere. The dimension of the cylindrically shaped crystals is about 5 × 5 × 20 mm^3. It is expected that Sr and Ca are distributed homogeneously in $Sr_{14-x}Ca_xCu_{24}O_{41}$ since the lattice constants systematically change and the linewidth of the nuclear Bragg peaks does not change when the ratio of Sr and Ca is changed. The lattice constants of $Sr_{11}Ca_3Cu_{24}O_{41}$ and $Sr_8Ca_6Cu_{24}O_{41}$ at 9 K are b=13.169 $\mathring{A}$ and c=27.448 $\mathring{A}$ and b=12.951 $\mathring{A}$ and c=27.381 $\mathring{A}$, respectively. These lattice constants are consistent with those obtained with powder samples. [5]

The neutron scattering experiments were carried out on the H8 spectrometer installed at the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory. The horizontal collimator sequences were $40'$-$40'$-S-$40'$-$80'$. The final neutron energy was fixed at E_f=14.7 meV. Pyrolytic graphite (002) was used as monochromator and analyzer. Contamination from higher-order beam was effectively eliminated using pyrolytic graphite filters after the sample. The single crystals were mounted in a closed cycle refregirator and were oriented in the $(0, k, l)$ scattering plane. As described in Ref. [1], there are three different values for the lattice constant c ($c_{\mathrm{universal}}$=10 × c_{chain}=7 × c_{ladder}). Since we will show the magnetic properties in the chain, c_{chain} will be used to express Miller indices.

III. RESULTS AND DISCUSSION

Figure 2 shows typical inelastic neutron spectra at (0,3,L) measured at 9 K in $\mathrm{Sr}_{14-x}\mathrm{Ca}_x\mathrm{Cu}_{24}\mathrm{O}_{41}$ (x=3 and 6). The magnetic excitation peaks become broad with Ca substitution, which is similar to the case of Y substitution. [15,19] It is noted that the two excitation branches (acoustic and optic), which are observed in pure $\mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{41}$ are hardly resolved. The peak width in the x=6 sample is broader than that in the x=3 sample, suggesting that the dimerized state become more unstable with Ca substitution. However, the excitation energies in the two samples are similar to those in pure $\mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{41}$. The solid lines at $(3,0,-0.07)$ and $(3,0,-0.21)$ are fits to a single Gaussian and that at $(3,0,-0.35)$ is a fit to two Gaussians by assuming that the dispersion relation is the same as that in $\mathrm{Sr}_{14}\mathrm{Cu}_{24}\mathrm{O}_{41}$ [18] as show in Fig. 1(d). A single Gaussian was used to fit the data at $(3,0,-0.07)$ and $(3,0,-0.21)$ because the intensities from the optic mode excitation are expected to be very small. [18] The spectra are reasonably described with the simple model. The averaged excitation energy, the band width of each excitation mode, and the energy difference between the acoustic and optic modes are related with J, J_c, and J_a, respectively. [18] Here, J, J_c, and J_a represent intradimer coupling, interdimer coupling in the same chain, and interdimer coupling between the adjacent chains, respectively, as shown in Fig. 1(c). This indicates that the coupling constants J, J_c, and J_a are almost unchanged with Ca substitution although the dimerized state becomes unstable. This behavior would be explained as follows. The hole ordering sensitively depends on the hole number. Accordingly, the long-range dimer formation becomes disturbed with Ca or Y substitution.

Figure 3 shows energy-integrated intensities as a function of L in the x=3 and 6 samples. The intensities of both samples show similar L dependence. There is a broad maximum around L=0.25, indicating that the dimers are formed between Cu spins which are separated by two times the distance between the nearest-neighbor Cu ions in the chain. Thus, the dimerized state in the Ca substituted system is considered to be similar to that in pure $Sr_{14}Cu_{24}O_{41}$ although the dimerized state becomes unstable.

In order to compare the results of the Ca substituted system with those of the Y substituted system, an inelastic neutron spectrum in $Sr_{13.5}Y_{0.5}Cu_{24}O_{41}$ is shown in Fig. 4. The width of the excitation peak is similar to that in the x=3 or 6 sample. However, the excitation energy is decreased to ~9 meV in the Y substituted sample while it is not affected (~10 meV) with Ca substitution. This result suggests that J is almost unchanged with Ca substitution but it is decreased with Y substitution. A puzzling feature is that J is decreased in $Sr_{13.5}Y_{0.5}Cu_{24}O_{41}$ although the lattice constant c, which affects the exchange constant, is almost independent of Y concentration. [20] On the other hand, the lattice constant c is slightly decreased with Ca concentration, [5] which is expected to increase J.

The dimerized state sensitively depends on the hole concentration in the chain. Since the hole concentration in $Sr_{14-x}Y_xCu_{24}O_{41}$ can be controlled, it is possible to estimate how much holes are transferred from the chains to the ladders in $Sr_{14-x}Ca_xCu_{24}O_{41}$ by comparing the magnetic properties of the two systems. The width of the excitation peak would be one of the parameters which change with Y or Ca substitution. It was concluded that the number of holes in the chain in $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x \sim 4.5$) is almost equal to that in $Sr_{13.5}Y_{0.5}Cu_{24}O_{41}$, in which 0.5 hole is removed from the chain compared with the number of the holes ~6 per 10 Cu ions in the chain in pure $Sr_{14}Cu_{24}O_{41}$. This is consistent with the results of the optical conductivity measurements. [7]

ACKNOWLEDGMENTS

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REFERENCES

[1] E. M. McCarron, III, M. A. Subramanian, J. C. Calabrese, and R. L. Harlow, Mat. Res. Bull. **23**, 1355 (1988).

[2] T. Siegrist, L. F. Schneemeyer, S. A. Sunshine, J. V. Waszczak, and R. S. Roth, Mat. Res. Bull. **23**, 1429 (1988).

[3] E. Dagotto and T. M. Rice, Science **271**, 618 (1996).

[4] R. S. Eccleston, M. Azuma, and M. Takano, Phys. Rev. B. **53**, R14721 (1996).

[5] M. Kato, K. Shiota, and Y. Koike, Physica C **258**, 284 (1996).

[6] Y. Mizuno, T. Tohyama, and S. Maekawa, J. Phys. Soc. Jpn. **66**, 937 (1997).

[7] T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **78**, 1980 (1997).

[8] N. Motoyama, T. Osafune, T. Kakeshita, H. Eisaki, and S. Uchida, Phys. Rev. B **55**, 3386 (1997).

[9] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori, and K. Kinoshita, J. Phys. Soc. Jpn. **65**,2764 (1996).

[10] K. Kumagai, S. Tsuji, M. Kato, and Y. Koike, Phys. Rev. Lett. **78**, 1992 (1997).

[11] K. Magishi, S. Matsumoto, Y. Kitaoka, K. Ishida, K. Asayama, M. Uehara, T. Nagata, and J. Akimitsu, Phys. Rev. B **57**, 11533 (1998).

[12] T. Imai, K. R. Thurber, K. M. Shen, A. W. Hunt, and F. C. Chou, Phys. Rev. Lett. **81**, 220 (1998).

[13] M. Matsuda and K. Katsumata, Phys. Rev. B **53**, 12201 (1996).

[14] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[15] M. Matsuda, K. Katsumata, H. Eisaki, N. Motoyama, S. Uchida, S. M. Shapiro, and G. Shirane, Phys. Rev. B **54**, 12199 (1996).

[16] M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B **57**, 1124 (1998).

[17] R. S. Eccleston, M. Uehara, J. Akimitsu, H. Eisaki, N. Motoyama, and S. Uchida, cond-mat/9711053.

[18] M. Matsuda, T. Yoshihama, K. Kakurai, and G. Shirane, Phys. Rev. B (submitted).

[19] M. Matsuda, K. Katsumata, H. Eisaki, N. Motoyama, S. Uchida, T. Yokoo, S. M. Shapiro, G. Shirane, and J. L. Zarestky, Phys. Rev. B **56**, 14499 (1997).

[20] M. Kato, T. Adachi, and Y. Koike, Physica C **265**, 107 (1996).

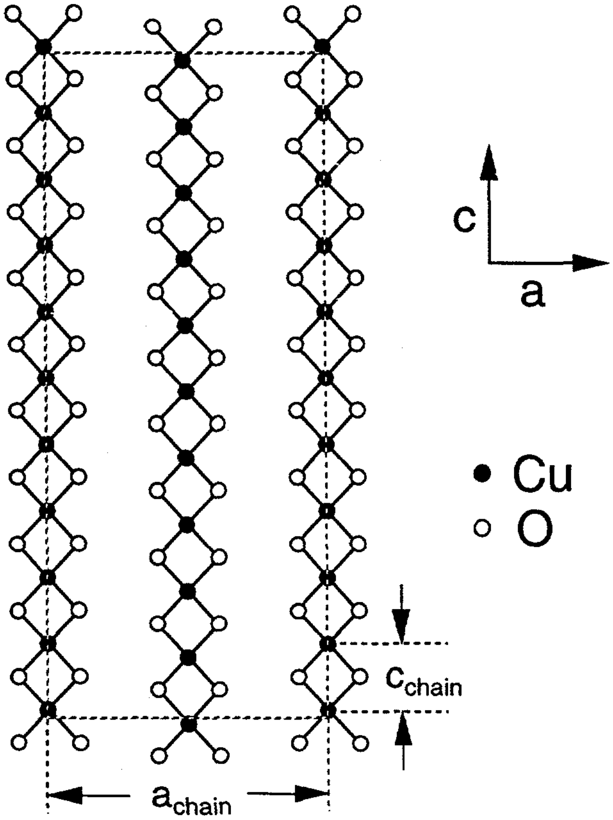
FIGURES

FIG. 1. Structure of the CuO_2 chains (a) and the Cu_2O_3 ladders (b) in $Sr_{14}Cu_{24}O_{41}$. Lower figures show a two-dimensional hole ordering model (c) and the dispersion relation in $Sr_{14}Cu_{24}O_{41}$ (d) obtained in Ref. 17.

FIG. 2. Typical inelastic neutron spectra at $(0,3,L)$ at 9 K in $Sr_{14-x}Ca_xCu_{24}O_{41}$ (x=3 and 6). The solid lines are the results of fits to a single Gaussian or two Gaussians.

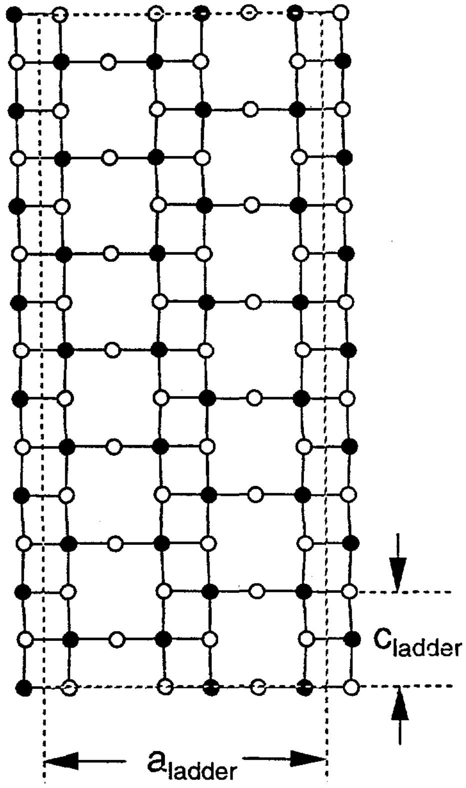
FIG. 3. Energy-integrated intensities at $(0,3,L)$ measured at 9 K in $Sr_{14-x}Ca_xCu_{24}O_{41}$ (x=3 and 6).

FIG. 4. An inelastic neutron spectra at (0,3,-0.35) at 11 K in $Sr_{13.5}Y_{0.5}Cu_{24}O_{41}$. The solid lines are the results of fits to a single Gaussian.



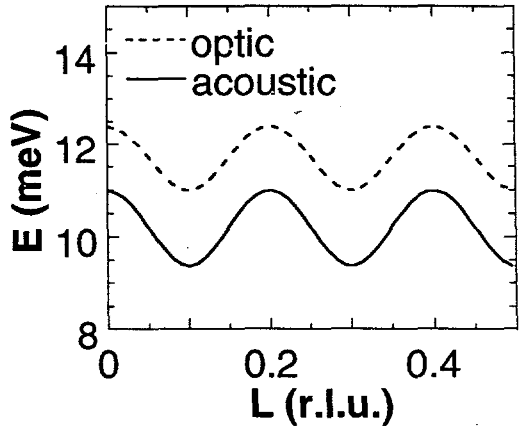
chain

(a)

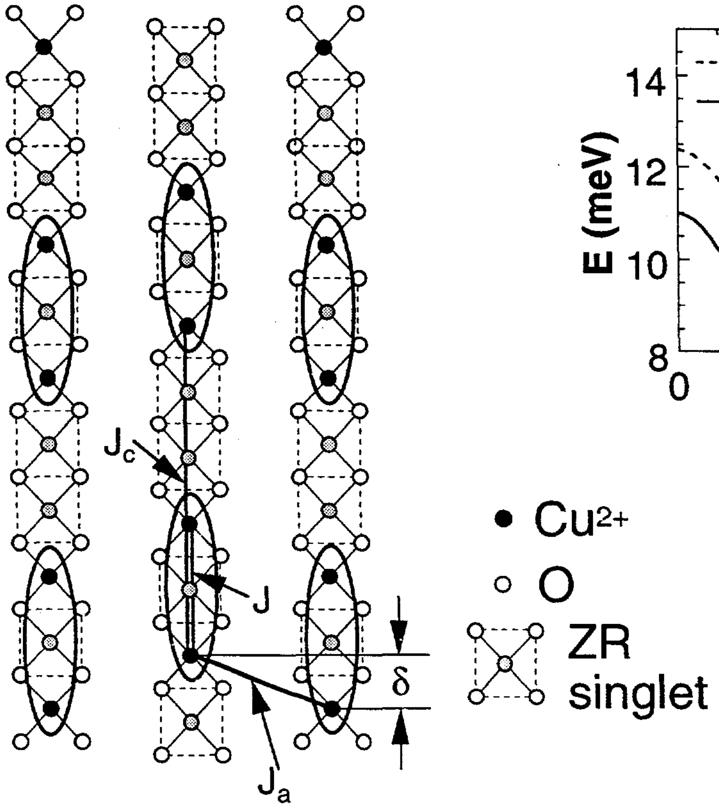


ladder

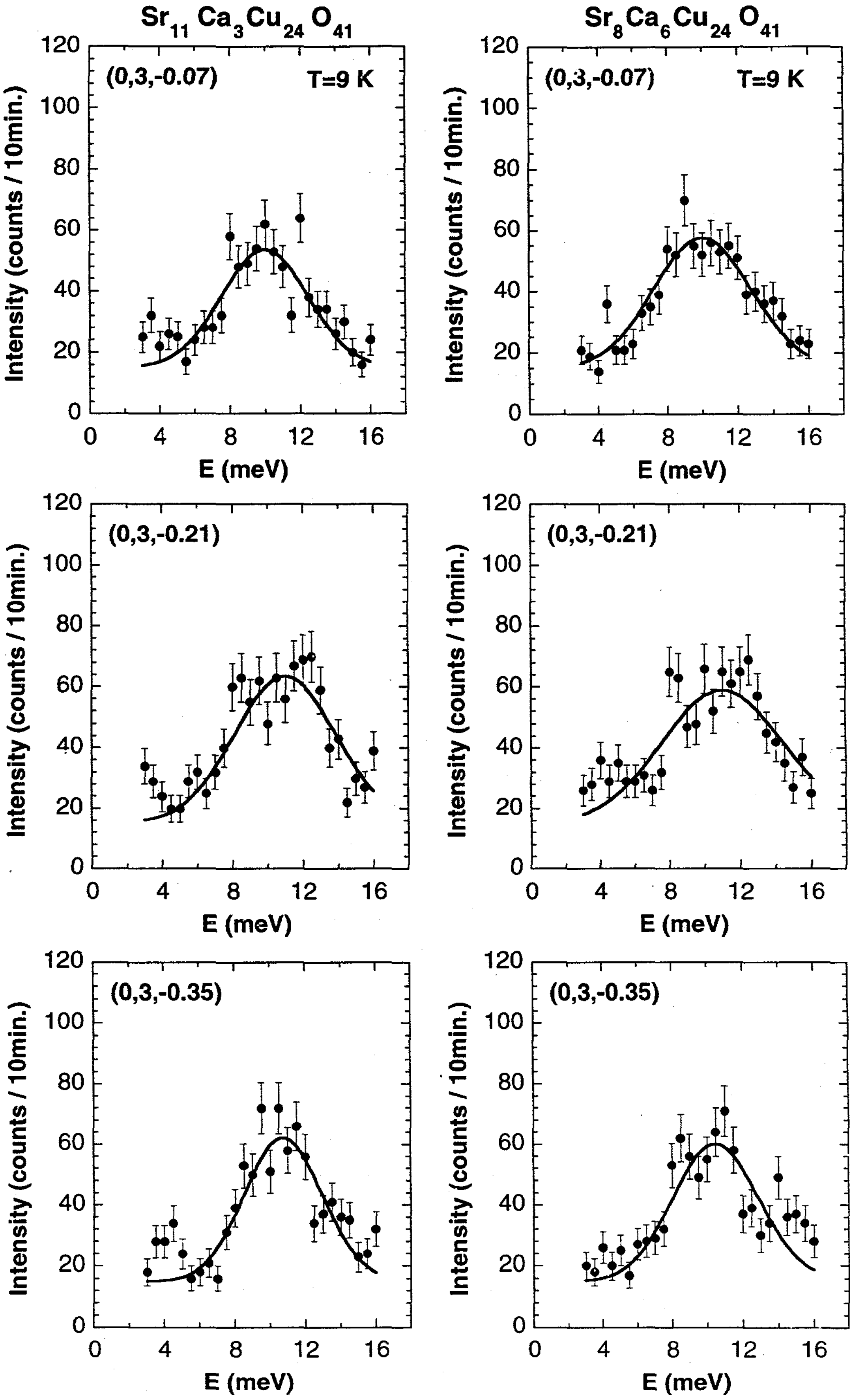
(b)



(d)



(c)


$Sr_{11}Ca_3Cu_{24}O_{41}$
$Sr_8Ca_6Cu_{24}O_{41}$
(0,3,-0.07)
T=9 K
(0,3,-0.07)
T=9 K
(0,3,-0.21)
(0,3,-0.21)
(0,3,-0.35)
(0,3,-0.35)
Intensity (counts / 10min.)
E (meV)
0
20
40
60
80
100
120
0
4
8
12
16

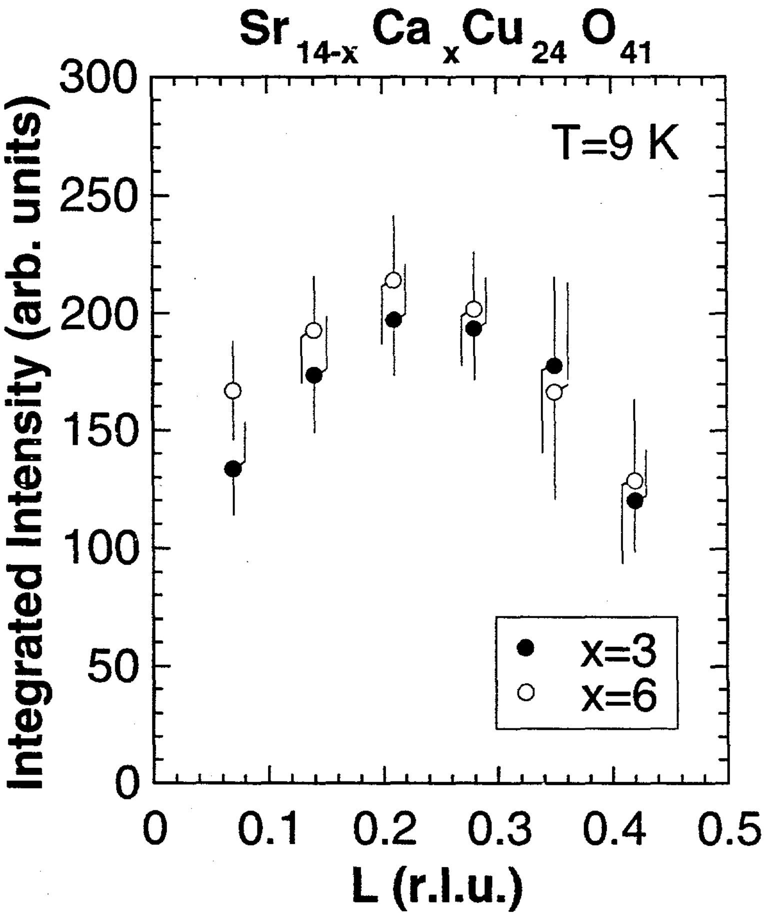


Fig. 3. Matsuda et al.

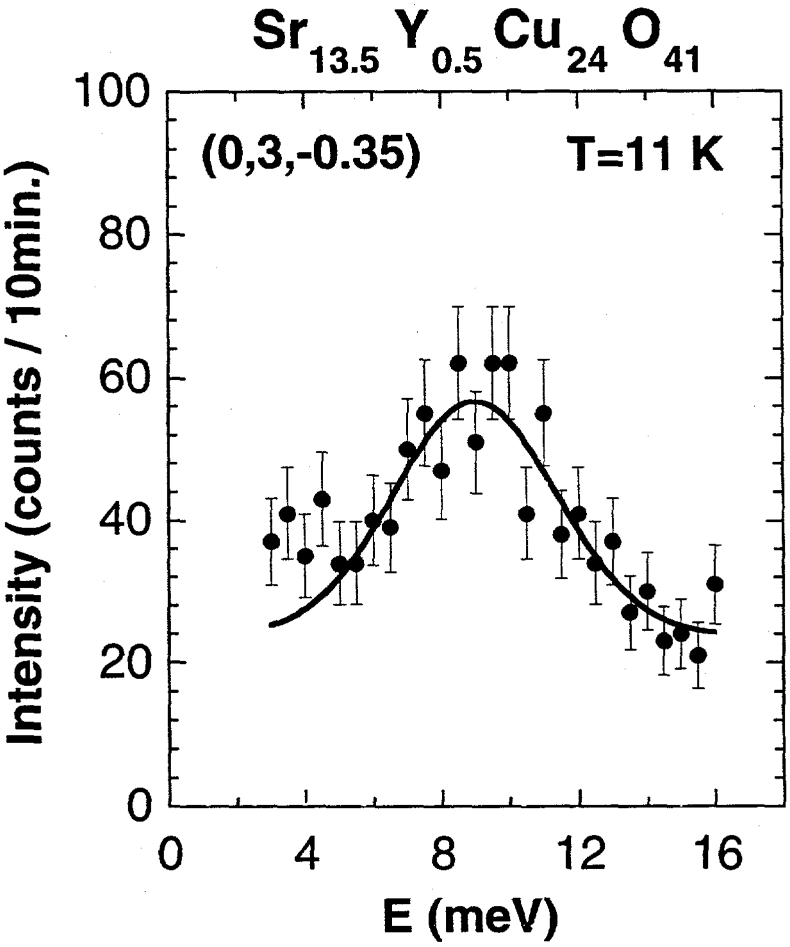


Fig. 4. Matsuda et al.