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SUSCEPTIBILITY MAGNETIC AND HIGH MAGNETIC FIELD ESR MEASUREMENT OF $SrCu_2(PO_4)_2$

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Abstract

The magnetic susceptibility and high magnetic ESR measurement of $SrCu_2(PO_4)_2$ has been performed at temperatures ranging from 4.2 K to 300 K and 4.2 K to 77 K, respectively. The magnetic susceptibility shows a broad maximum around T = 40 K. The magnetic susceptibility has been interpreted in terms of one-dimensional magnetic systems. The temperature dependence of the magnetic susceptibility indicated a good agreement with 4-spin alternating configuration model. In the ESR measurement, clear electron spin resonance (ESR) was observed. The integrated intensity for 120 and 301 GHz has a broad maximum at around 40 K, which is consistent with the susceptibility result. A quantitative description gives resonance is the first and second triplet excited states of the excitation spectrum of 4-spin alternating chain configuration. The g_1, g_2 and g_3 values are approximately 2.21 at temperature above 40 K. The g_2 dan g_3 values have the dependence of temperature under 40 K.

Keywords: magnetic susceptibility, electron spin resonance, singlet ground state, triplet excited states, 4-spin alternating chain

1. Introduction

The alternating chain is interesting as a simple 1D isotropic quantum spin systems with a gap. This is similar to other systems such as integer-spin chains conjectured by Haldane [1], isolated-AF dimer $CaCuGe_2O_6$ [2], even-leg $S = 1/2$ spin ladders $(VO)_2P_2O_7$ [3-4], NaV_2O_5 [5] and $SrCu_2O_3$ [6]. These discoveries have marked development in the field of quantum spin systems.

Inspired by discovery the alternating chains in $CuWO_4$ [7], $Sr_{14}Cu_{24}O_{41}$ [8], α'-NaV_2O_5 [9] and $CuGeO_3$ [10], we directed our attention to $M$$Cu_2(PO_4)_2$ (M = Ba, Sr) with magnetic ions. The crystallographic structure $SrCu_2(PO_4)_2$ is triclinic with space group and unit cell constants a = 9.226 Å, b = 9,271 Å, c = 10,516 Å, α = 106.76°, β = 101.65°, and γ = 115.70° [11-12]. The structure of $SrCu_2(PO_4)_2$ is nearly identical to that of $BaCu_2(PO_4)_2$ at room temperature [13-14]. The main feature of the crystal structure is $[CuPO_4]^n{}_n$ sheets linked together by the Ba^{2+} or Sr^{2+} cations parallel to the (001) direction. In each $(CuPO_4)$ layer, the Cu atoms isolated by the (PO_4) tetrahedral constitute magnetic chains and structure contains a one dimensional S = ½ Heisenberg spin chains.

It is very interesting to investigate 1D magnetic properties of $M$$Cu_2(PO_4)_2$ (M = Ba, Sr). Susceptibility magnetic of $BaCu_2(PO_4)_2$ and $SrCu_2(PO_4)_2$ powders have confirmed these compound to be a good 1D spin-1/2 Heisenberg antiferromagnetic (AF) chain system. The susceptibility of $BaCu_2(PO_4)_2$ shows a broad peak around 60 K and claimed it originated from the ladder chain [13-14], while $SrCu_2(PO_4)_2$ shows broad peak about 40 K and originated from

4-spin alternating chain [11]. In the ESR measurement, the first triplet state of the excitation magnetic of ladder configuration in $BaCu_2(PO_4)_2$ was observed [14]. There seems to be a significant different in formation singlet ground state between $BaCu_2(PO_4)_2$ and $SrCu_2(PO_4)_2$. Therefore, detailed studies of the mechanism for formation singlet ground state in $SrCu_2(PO_4)_2$ are clearly needed. For this purpose, magnetic susceptibility was reexamined to confirm the correct interpretation of the existence of a spin singlet ground state with an energy gap in $SrCu_2(PO_4)_2$. Further, electron spin resonance (ESR) was performed on $SrCu_2(PO_4)_2$ powder to observe the transitions between the singlet ground state and the excited triplet.

2. Methods

$SrCu_2(PO_4)_2$ sample powder was prepared from appropriate mixtures of the source materials, $(NH_4)_2HPO_4$, $SrCO_3$, and CuO in a molar ratio 2:1:2. The mixtures were heated at 900^0C for 15 hours in an evacuated silica tube and cooled to 800^0C. To complete the chemical reaction, the resulting product was reacted with repeated procedure until X-ray diffraction indicated the existence of a single-phase.

Magnetic properties of $SrCu_2(PO_4)_2$ powder were studied by magnetic susceptibility and electron spin resonance (ESR) measurements. Magnetic susceptibility was measured using a Quantum Design Superconducting Quantum Interference (SQUID) device magnetometer in the $4.2\ K \le T \le 300\ K$ temperature range. Approximately 10 mg of sample were placed in a sealed quartz tube of 3 mm in diameter filled with 10% H_2/Ar gas. In the magnetometer, magnetic susceptibility vs temperature curves were obtained by applying a magnetic field of 1 T.

ESR measurement was performed by a submillimeter wave ESR spectrometers using high pulse magnetic of 35 T, temperature control from 4 K to 300 K, and Gyrotron and Gunn Oscillator as a radiation source. The electromagnetic wave was transmitted through a sample placed at the center of the pulse magnet. The transmitted wave was detected by an InSb hot electron detector. The detected signal is amplified by a low noise amplifier. The output signal and signal from the pick up coil for field measurement were recorded by two channel digital memory oscilloscope and then fed to a computer.

We have used a pulse magnet generating high magnetic field up to 35 T. The measurement of magnetic field intensity was made by integration of the induced voltage from the pick up coil. The pulse magnet system has the field intensity pattern similar to a half sinusoidal one with the width of 2.5 ms.

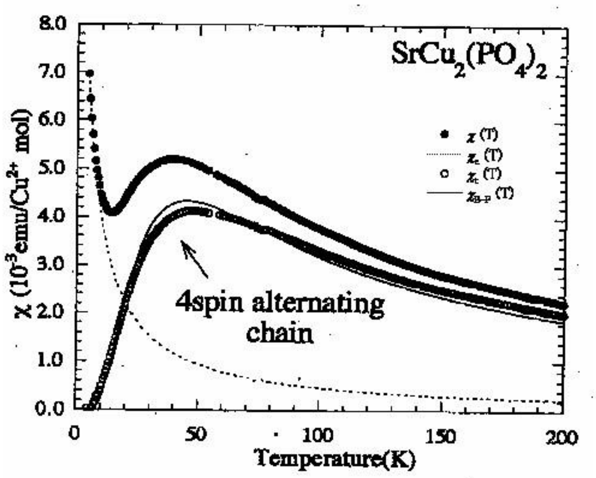


Figure 1. The temperature dependence of magnetic susceptibility of $SrCu_2(PO_4)_2$ measured 1.0 T

$SrCu_2(PO_4)_2$ and DPPH powder were set in a sample holder, which placed at the center of the pulse magnet. DPPH powder was used as a standard sample with g = 2.0023. The temperature was measured by a FeAu 0.07 at.%-Ag thermocouple. The measurements were performed from 4 K to 77 K. All preparation and experiments were carried out in Research Center for Development of Far Infrared Region, and Department of Applied Physics, Faculty of Engineering, Fukui University, Japan.

3. Results and Discussion

Result of Magnetic Susceptibility Measurement. Figure 1 shows the temperature dependence of magnetic susceptibility of $SrCu_2(PO_4)_2$ measured at 1 T. Solid circles, dashed curve, open circles, and solid curve represent the measured susceptibility , the susceptibility to impurities , and the theoretical susceptibility , respectively. The susceptibility shows a broad maximum at around 40 K, a characteristic of a low dimensional antiferromagnets, and decreases rapidly with decreasing temperature.

In order to analyze the susceptibility quantitatively, the Curie term is eliminated in . It is assumed that the spins to impurities of Cu^{2+} ions are isolated spins. Thus the data below 10 K were fitted to Curie-Weiss susceptibility , where is the curie constant and is the Weiss temperature. The magnetic susceptibility is fitted numerically by [16]:

(1)

where is the Boltzmann constant and . The coefficients are given by , , , and . The *B-F* is a function of , so that is estimated to be 0.75. The , and *g* parameters were estimated as 40 K, 30 K, and *g* = 2.24, respectively.

The theoretical curve agrees well with qualitatively. This agreement indicates that the magnetic properties of $SrCu_2(PO_4)_2$ can be explained approximately by the spin system with 4-spin alternating-chain model. The 4-spin alternating-chain model configuration is shown in Figure 2.

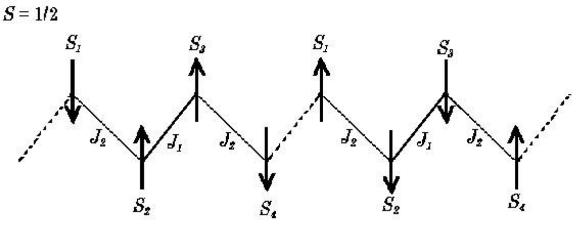
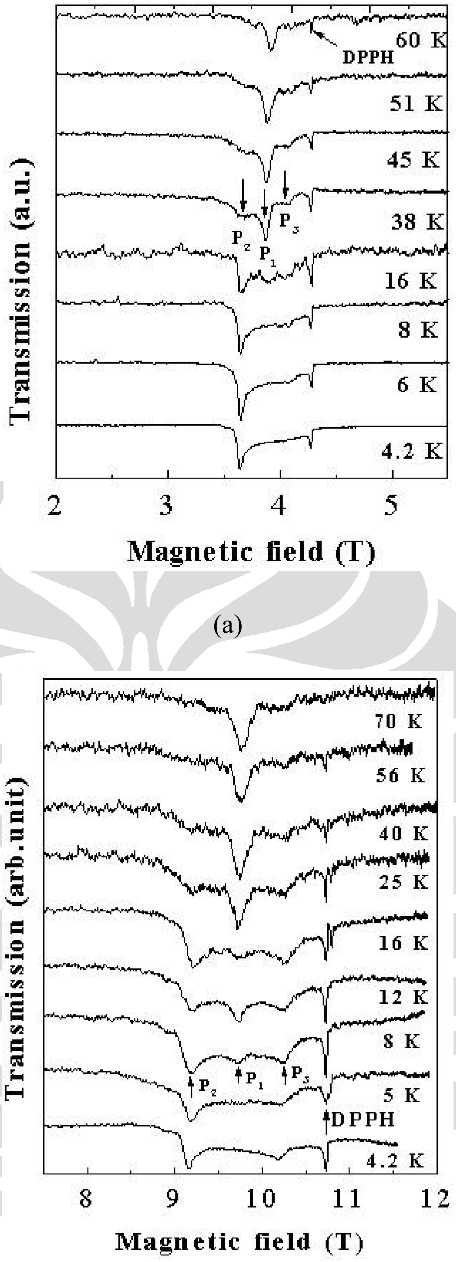


Figure 2. Schematic Cu^{2+} ion configurations in $SrCu_2(PO_4)_2$



(a)

(b)

Figure 3. Temperature dependence of resonance observed at (a) 120 GHz and (b) 301 GHz. P_1, P_2, and P_3 stand for three resonance absorption lines.

Result of Electron Spin Resonance (ESR) Measurement. The ESR measurement for 4.2 K to 60 K and 4.2 K to 70 K in $SrCu_2(PO_4)_2$ powder for two different frequencies is presented. Fig. 3a and 3b show the temperature dependence of the ESR line observed at 120 and 301 GHz, respectively. Below 40 K we observe three resonance lines P_1, P_2, P_3, while above 40 K, one resonance line P_1 is observed. The resonance P_1 at H = 9.7 T increases its intensity as the temperature is increased up to 40 K, while its linewidth decreases continuously. When the temperature is increased further, the intensity of the resonance P_1 decreases. As the temperature is decreased, one resonance line P_2 shifts towards lower field and another one P_3 shifts towards higher field.

Figure 4 and 5 show the integrated intensity of P_1, P_2, P_3 absorption lines as a function of the temperature for 120 GHz and 301 GHz. For the ESR intensity, we used the 4-spin (S=1/2) alternating-exchange-interaction chains model, which gives the equation [15]:

, (2)

with,

,

,

where,

,

,

where k_B and *H* represent Boltzmann's constant and the applied magnetic field, respectively.

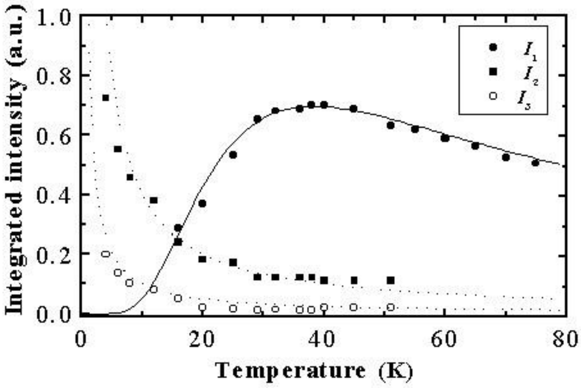


Figure 4. Temperature dependence of the integrated intensity at 120 GHz. Closed, open circles and close square denote the measured intensity for I_1, I_3 and I_2. The solid curve represents the calculated result.

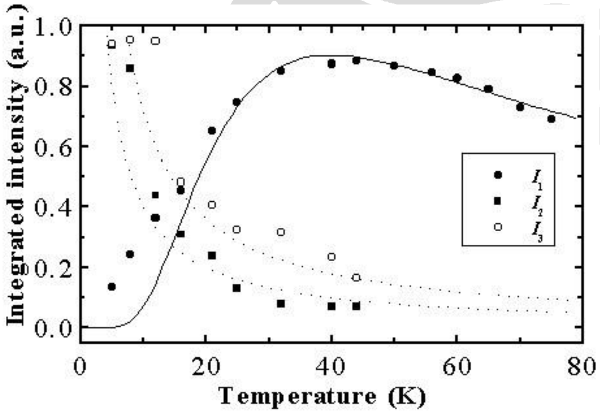


Figure 5. Temperature dependence of the integrated intensity at 301 GHz. Closed, open circles and close square denote the measured intensity for I_1, I_3 and I_2. The solid curve represents the calculated result.

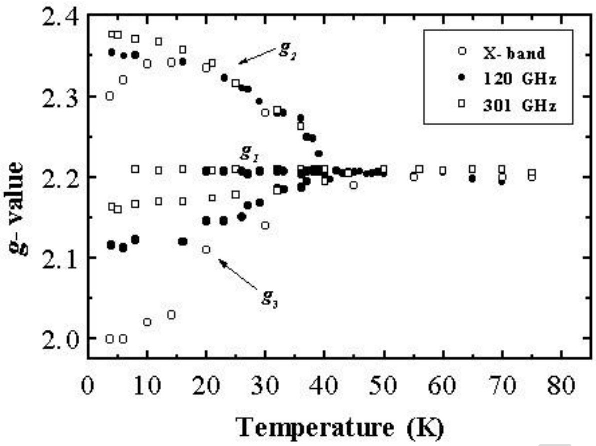


Figure 6. Temperature dependence of *g*-values. Opened circles, closed circles and opened squares stand for the g-values at X-band$^{11)}$, 120 GHz and 301 GHz, respectively.

The solid line in Fig. 4 and 5 is a fit to the experiment with the parameters as follows: E_{02} = -2605 GHz, E_{01} = 416 GHz, E_{13} = -1354 GHz, E_{12} = 729 GHz, E_{11} = -521 GHz, and E_{21} = 1146 GHz and the corresponding magnetic field H = 9.7 T for the frequency of 301 GHz and H = 3.5 T for frequency of 120 GHz.

Since is defined by Hase [15], we can determine the values of dan , so as to make the temperatures at maximum I_1(T) and the calculated result coincide with each other. Qualitatively, the calculated result agrees well with the experimental result. The temperatures dependence of the integrated intensity indicated that we observe transitions in the singlet ground state, first and second triplet excited states. The ESR intensity I_1(T) has a broad peak about 40 K. Below 40 K, the intensity I_1 start to decrease rapidly for all frequencies as temperature is decreased, which is consistent with the susceptibility result. A quantitative description gives resonance is the first and second triplet excited states of the excitation spectrum of 4-spin alternating chain configuration. The results of the experiments are all in good agreement with theory.

Fig. 6 shows the temperature dependence of g-value of $SrCu_2(PO_4)_2$. The g_1, g_2 and g_3 values are g-value for the absorption lines P_1, P_2 and P_3, respectively. The g_1, g_2 and g_3 values are approximately 2.21 at temperature above 40 K. The g_2 value increases and the g_3 value decreases at temperature under 40 K.

4. Conclusion

Magnetic susceptibility and high magnetic field ESR measurements of $SrCu_2(PO_4)_2$ have been performed at temperatures from 4.2 K to 300 K and 4.2 K to 77 K, respectively. The temperature dependence of the magnetic susceptibility indicated a good agreement with 4-spin alternating configuration model. In the ESR measurement, clear electron spin resonance (ESR) was observed. The integrated intensity for 120 and 301 GHz has a broad maximum at around 40 K, which is consistent with the susceptibility result. A quantitative description gives resonance is the singlet ground state, first and second triplet excited states of the excitation spectrum of 4-spin alternating chain configuration. The g_1, g_2 and g_3 values are approximately 2.21 at temperature above 40 K. The g_2 dan g_3 values have temperature dependence below 40 K.

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