High field ESR measurement of diamond chain substance $Cu_3(OH)_2(CO_3)_2$

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Abstract

Azurite, $Cu_3(OH)_2(CO_3)_2$ is a candidate of the model substance for diamond chain with antiferromagnetic interaction. The millimeter and submillimeter wave ESR measurements of $Cu_3(OH)_2(CO_3)_2$ single crystal have been performed in the frequency region from 50GHz to 360GHz and in the temperature region from 1.8K to 90K. As the linewidth of ESR extends up to 3T and it is impossible to observe by a conventional X-band ESR, the high field ESR measurement turned out to be essential. The g-shift was observed below 20K, which corresponds to a peak of the magnetic susceptibility. Therefore, the development of the short range order may be the origin of the resonance shifts.

Key words: $Cu_3(OH)_2(CO_3)_2$; diamond chain; antiferromagnet; ESR

Recently, low dimensional quantum spin systems have attracted much attention due to the discovery of model substances. $Cu_3(OH)_2(CO_3)_2$, which is known as a natural mineral Azurite and the space group is C_{2h}^5 and the chain direction is the b axis, can be considered as a model substance for one dimensional (1D) diamond chain. Takano *et al.* investigated analytically the ground state for S=1/2 diamond chain [1]. There are three ground state phases for λ=J'/J, such as the ferrimagnetic (FM) phase, the tetramer-dimer (TD) phase, and the dimer-monomer (DM) phase. From the magnetic susceptibility and magnetization measurements [2], Azurite can be considered as the model substance of one dimensional diamond chain for DM phase. From proton NMR measurements, T_N was estimated to be 1.86K [3]. Although most of the magnetic measurements of Azurite were performed in '50-'60, the dynamical property of $Cu_3(OH)_2(CO_3)_2$ is little known. Therefore, to investigate the dynamical properties of the 1D diamond chain we have performed the high field ESR measurements of Azurite single crystal using the pulsed magnetic field up to 16T. The observed temperature region was from 1.8K to 90K, and the frequency region was from 50GHz to 360GHz. The details of our ESR system can be found in refs. [4,5].

We performed the ESR measurements at 90K and estimated the g-values of Azurite for the paramagnetic region, which are g=2.098, 2.128, 2.110 for the magnetic field parallel to the a, b, and c axes respectively. Figure 1 shows the temperature dependence of the g-values for H//a, b (chain), and c axes. Although the g-values for H//b and c become smaller and larger below 20K, respectively, which corresponds to the temperature of the peak of the magnetic susceptibility [2], the g-values for H//a are almost constant in the observed

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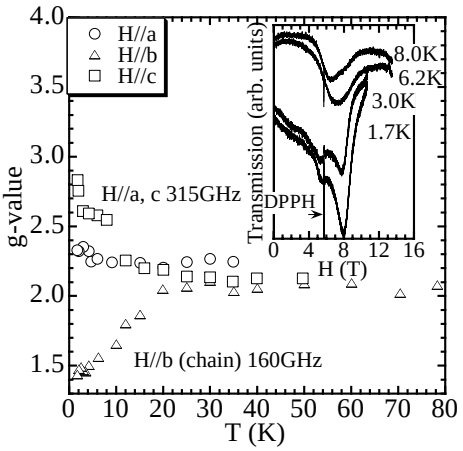

Fig. 1. The temperature dependence of g-value for H‖a (○), ‖b (△), and ‖c (□) axes. The inset shows the temperature dependence of the ESR spectra for H‖b observed at 160GHz. The resonance near the DPPH is the impurity, malachite.

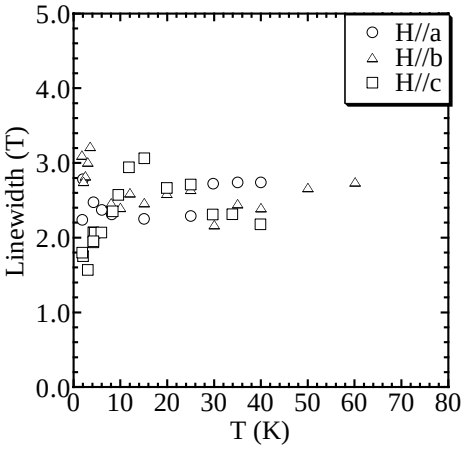

Fig. 2. The temperature dependence of the linewidths observed at 160GHz.

temperature region. We think the resonance shifts below 20K indicate the development of short range order. The behavior of the resonance shifts, however, for the magnetic field parallel and perpendicular to the chain direction are quite opposite to the behavior of the resonance shifts of the $CsMnCl_32H_2O$ [6,7], which is well known as the one-dimensional Heisenberg antiferromagnet. Here, we want to point out that the malachite $Cu_2(OH)_2(CO_3)$ is easy to aggregate with the natural mineral Azurite $Cu_3(OH)_2(CO_3)_2$. To select single phase Azurite, we checked the diffraction pattern by the X-ray diffraction measurements. We think the resonance near the DPPH, which is shown in the inset of Figure 1, is due to the impurity malachite. Figure 2 shows the temperature dependence of the linewidths. They are taken as 2 times of half width at half maximum of the ESR absorption because the absorption lines are asymmetric. As shown in the inset of Figure 1, the linewidths are very broad, and the high field ESR measurement is necessary to observe the absorption lines. The linewidths for H//b and c become broader and sharper below 10K, respectively, while the linewidths for H//a are almost constant in the observed temperature region. Although the typical low dimensional antiferromagnet shows divergence of the linewidth at low temperature, we did not observe such behavior. It is noted that the absorption lines at 8.0K and 6.2K in the inset of Figure 1 seem to have a shoulder respectively. Although we assumed that the absorption line has one resonance in the present study, it might be better to regard the absorption lines as the coexistence of two absorption lines considering the large g-shifts and the behavior of the linewidths. If we look at the temperature dependence of the absorption lines that way, one absorption line develops above 8K, while the another absorption line develops below 8K. And the two absorption lines seem to coexist around 8K. In ordre to check this point, high field ESR measurement beyond 315GHz is required.

In summary, high field ESR measurement of diamond chain substance $Cu_3(OH)_2(CO_3)_2$ is performed. The high field ESR measurement turned out to be essential due to its very broad linewidth.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (B) (No. 13130204 "Field-Induced New Quantum Phenomena in Magnetic Systems") from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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