Supplementary Information

for

Magnetic ordering of spin systems having fractal dimensions — Experimental study

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1 Characterization of AKD

(a) and (b) SEM images of AKD after heating (melting) and re-solidifying: (a) ×5000, (b) ×7000 (yellow scale bars indicate 2 µm in both (a) and (b)), and (c) chemical structure of AKD: R = n-C₁₆H₃₃ (R₁) or n-C₁₄H₂₉ (R²). Commercially available AKD is a mixture of R₁:R² = 3:4:7-6. As for (a) and (b), note that similar photographs are always obtained after grinding AKD at room temperature instead of heating/melting, and irrespective of magnification.

Figure S1. SEM images of AKD after heating (melting) and re-solidifying: (a) ×5000, (b) ×7000 (yellow scale bars indicate 2 µm in both (a) and (b)), and (c) chemical structure of AKD: R = n-C₁₆H₃₃ (R₁) or n-C₁₄H₂₉ (R²). Commercially available AKD is a mixture of R₁:R² = 3:4:7-6. As for (a) and (b), note that similar photographs are always obtained after grinding AKD at room temperature instead of heating/melting, and irrespective of magnification.
Figure S2. Thermal properties of AKD used in this study; (a) differential scanning calorimetry (DSC), and (b) thermogravimetric differential thermoanalysis (TG-DTA).
2 Details of how to determine $D$ from SANS and USANS

2.1 Light scattering by fractal bodies

There are some experimental methods established to determine the $D$ of a given geometry [S1]. Among them the measurement of the intensity of coherent photons scattered by fractal bodies are powerful methods to determine the $D$ of bulk samples having $D > 2$. Fractal bodies consist of self-similar smaller parts and the size (scale) of the smaller parts ranges more than 2-3 orders of magnitudes. Accordingly SANS and USANS have advantage over other light scattering experiments because by far the widest range of wavelength (matter wave) is available. Here the outline of how to determine $D$ from SANS and USANS is described [S2].

For simplicity, here we assume that an AKD/CoO mixed powder sample can be regarded as an aggregation (called “fractal cluster” below), which is comprised of small parts (about an order of 10 nm-1 µm diameter) of AKD/CoO mixture having various sizes. Now we should assume that the fractal cluster consists of $N$ pieces of small parts (radius $\sim a$) and the cluster’s “effective radius” can be approximated as the radius of gyration $R_g$, defined as follows.

$$N \sim R_g^D$$

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (r_i - r_c)^2}$$

$$r_c = \frac{1}{N} \sum_{i=1}^{N} r_i$$

where $N$ is the total number of constituents (the small parts of the fractal cluster), $r_i$ is the position vector of $i$-th constituent ($i = 1, 2, 3, \ldots, N$), and $r_c$ is the center of gravity of the fractal cluster. In short $R_g$ is the standard deviation of $r_i$. Here we should assume that (1) the scattering is elastic, and that (2) multiple scattering can be negligible. Both assumptions are valid when the energy of the sample excited by the scattering is small and scattering is weak. Both are true in most cases of SANS and USANS. The excitation energy is usually described by the momentum $\hbar q$;

$$q = k_s - k_i$$

$$q = |q|$$

where $q, k_s$ and $k_i$ indicate scattering, incident, and scattered wavenumber vectors,
respectively, and $q$ is the scattering wavenumber. The scattering mechanism qualitatively differs depending on the wavelength $\lambda$ of neutron beam as fractal bodies have different characteristic scales ($a$ and $R_g$), which can be larger than, comparable to, and smaller than the neutron wavelength $\lambda$. Thus we shall discuss the mechanism in the following three different cases.

### 2.2 Long $\lambda$ region ($\lambda \geq R_g$)

The scattering intensity $I(q)$ is proportional to the Fourier transformation of density correlation function $C(r)$.

$$S(q) = \int e^{iq \cdot r} C(r) dr$$

$S(q)$ contains structural information such as crystal structures. Hereafter the vector-character of $q$ can be ignored since the fractal cluster is rather isotropic. Now $\lambda \geq R_g$ (Figure S3), all the $N$ pieces of small parts should scatter the neutrons in a coherent way, since all the small parts are within a single wave and thus can be approximated to be in phase. Thus

$$I(q) \sim NS(q) \sim N \int e^{iq \cdot r} C(r) dr \quad (S2)$$

![Figure S3](image)

**Figure S3.** Scattering model for a fractal body smaller than $\lambda$.

Here

$$qR_g = \frac{2\pi}{\lambda} R_g \leq 1$$

and thus one can approximate as

$$|q \cdot r| \ll 1$$
Then Taylor expansion
\[ e^{iq \cdot r} = 1 + iq \cdot r - \frac{1}{2} (q \cdot r)^2 + \cdots \]
enables us to carry out the integration in (S2), and gives
\[ I(q) \sim N^2 \left( 1 - c q^2 R_g^2 + \cdots \right) \tag{S3} \]
where \( c \) is a constant (\( c \sim 1 \)). (S3) means that \( I(q) \) is independent of \( D \) when \( \lambda \geq R_g \).

2.3 Intermediate \( \lambda \) region \( (a < \lambda < R_g) \)

In this \( \lambda \)-region, one may consider that the fractal cluster should consist of parts having a diameter of \( \lambda \) (Figure S4). In the same parts all the small microparticles coherently scatter the neutrons, while different parts scatter them in an incoherent way to each other. Because of the self-similarity, such parts can still be regarded as a fractal cluster, and thus one can apply the same discussion above (§2-2).

Figure S4. Scattering model for intermediate \( \lambda \)-region.

The scattering intensity depends upon the following two factors; (1) the number of microparticles contained in the part, and (2) the number of parts having the characteristic scale \( \lambda \) in the sample. Firstly, we should consider the contribution of a single part to the scattering. In every single part there are the number of microparticles proportional to \( \lambda^D \) ((S1)) according to the definition of fractal dimension \( D \).
Thus the scattering intensity from the abovementioned single part is proportional to \((\lambda^D)^2\) by use of (S3) \((N = \lambda^D)\).

On the other hand, the incoherent scattering from different parts gives \(N\)-dependence of \(I(q)\) instead of \(N^2\)-dependence in (S3). Therefore, the total contribution of incoherent scattering is proportional to the number of parts itself, \(i.e. \left( \frac{R_g}{\lambda} \right)^D\), since \(R_g^D\) and \(\lambda^D\) are the volume in \(D\)-dimension of the original (whole) fractal cluster and that of the part, respectively. Accordingly, the net contribution to \(I(q)\) from both coherent and incoherent scatterings is given by

\[
I(q) \sim \left( \frac{R_g}{\lambda} \right)^D (\lambda^D)^2 \sim (R_g\lambda)^D \sim q^{-D}
\]  

(S4)

This result means that \(\log\{I(q)\} \) vs \(\log(q)\) plot gives a linear relation with the inclination of \((-D)\) when \(a < \lambda < R_g\). This is how one can know \(D\), more exactly mass fractal dimension \(D_m\), from the analysis of SANS and USANS.

2.4 Short \(\lambda\) region \((a > \lambda)\)

In this \(\lambda\)-region, the coherent parts of diameter \(\lambda\) is smaller than the size of microparticles. This means that neutrons are scattered at the surface of microparticles when they do not penetrate into the particles. In this case, one can consider that the microparticles should be covered with scatterers having a diameter of \(\lambda\) and \(D = 3\) (Figure S5). A single scatterer contains the number of atoms proportional to its volume \(\lambda^3\), and all the atoms in a scatterer coherently scatter neutrons.
**Figure S5.** Scattering model for a microparticle (radius = $a$) having surface fractal dimension $D_S$. Assume $\lambda < a$. Red circles indicate imaginary scatterers (diameter = $\lambda$) covering the microparticle.

Thus the contribution of a scatterer to $I(q)$ is proportional to $(\lambda^3)^2$. On the other hand, the number of scatterers at a microparticle surface is proportional to $\left(\frac{a}{\lambda}\right)^{D_S}$, where $D_S$ is the surface fractal dimension. As different scatterers should scatter neutrons incoherently, their contribution to $I(q)$ is proportional to $\left(\frac{a}{\lambda}\right)^{D_S}$. The total contribution of $N$ pieces of microparticles to $I(q)$ is described as follows;

$$I(q) \sim N \left(\frac{a}{\lambda}\right)^{D_S} (\lambda^3)^2 \sim N a^{D_S} \lambda^{6-D_S} \sim q^{D_S - 6} \quad (S5)$$

The equation (S5) means that log{$I(q)$} vs log{$q$} plot gives a linear relation with the inclination of $(D_S - 6)$ when $\lambda < a$. This is how one can know $D_S$ independent of $D$ (mass fractal dimension $D_m$) from the analysis of SANS and USANS.

Summarizing the results above, *i.e.* (S3)-(S5) in each $\lambda$-region, one can obtain a relation between log{$I(q)$} and log{$q$} as schematically shown below (**Figure S6**). In this work, actual analysis was carried out using a more sophisticated model, which can describe all these three $\lambda$-regions by a single fitting function and thus can eliminate the ambiguity originating from how we distinguish one $\lambda$-region from the others.
2.5 Experimental and results of SANS and USANS

2.5.1 Scattering experiments and results

USANS and SANS experiments were carried out using SANS-J-II and PNO beam lines in JRR-3 (Japan Research Reactor-3) of Japan Atomic Energy Agency (JAEA) (Proposal No. 2010A-A21), respectively. For each $D$-dimensional sample, 8–10 pellets of mixtures of CoO and AKD particles were examined (diameter 10 mm and thickness 1–2 mm). The pellets were put in the sample holder with quartz window (window size $3\times4$ cm$^2$).

Figure S7 shows the scattering results obtained by SANS. From the results, the following points can be found. (1) The scattering intensity increases with an increase in CoO vol% because CoO particles are strong scattering objects. (2) However, the slopes of the scattering intensities of samples containing $\geq 20$ vol% CoO decreases at $q \leq 2\times10^{-3}$ nm$^{-1}$ in comparison with those in $q = 2\times10^{-2} - 10^{-1}$ nm$^{-1}$. This is due to multiple scattering between CoO particles in long range. (3) In $q = 2\times10^{-2} - 10^{-1}$ nm$^{-1}$, the slopes of the scattering intensities slightly increases with CoO vol% from 1 vol% to 50 vol%
and finally become constant.

**Figure S7.** Scattering intensity of samples of by SANS and USANS experiments.

### 2.5.2 Fitting equation

Here, we utilized the modified Ornstein-Zernike (OZ) equation to determine mass fractal dimension $D_m$ and surface fractal dimension $D_s$.

\[
I(q) = I(0) \frac{1}{(1+\beta^2 q^2)^{\alpha}} \frac{1}{(1+\delta^2 q^2)^{\eta}}
\]

where $I(q)$ and $I(0)$ are the scattering intensities at arbitrary wave number $q$ and $q = 0$, respectively, $\alpha$, $\beta$, $\delta$ and $\eta$ are fitting parameters. In particular, the following relations are maintained in the modified OZ equation [S3, S4].

\[
D_m = 2\alpha \\
D_s = 6 - 2(\alpha + \eta)
\]
2.5.3 Fitting results

Figure S8 shows typical fitting results in the range of $0.0003 < q < 0.2 \text{ nm}^{-1}$ of the 100, 67, 33, 25, 20, and 5 vol% CoO samples from (a) to (f) in this order, respectively. The fitting curves represent the data very well. From the obtained $\alpha$ and $\beta$, the changes of $D_m$ and $D_s$ were evaluated. The former and the latter describe the distribution of CoO particles in the samples and the smoothness of the CoO domains, respectively.

Figure S8. Typical fitting results for CoO (a) 100, (b) 67, (c) 33, (d) 25, (e) 20, and (f) 5 vol%, respectively. The red lines represent fitting results.
3 Crystal and electronic structures of AKD/CoO mixtures

Figure S9. Powder X-ray diffraction pattern for AKD/CoO mixture. All the patterns are identical within an experimental error in terms of relative intensities, positions and linewidths of the diffraction peaks between samples with different $D$s.
Figure S10. Magnetic susceptibility (DC) of CoO/AKD mixture with various CoO contents in vol%. ○; field-cooling (FC), and □; zero-filed cooling (ZFC) data.
Figure S11. Reproducibility of $T_N$ among different measurements. All the samples are independently prepared having the same $D$ (2.50); (a) sintered compaction pellet, i.e. sample does not include AKD, (b)-(d) raw pellets/powder, i.e. samples include AKD. The arrow in (c) means an irreproducible (accidental) jump in ZFC process, which makes the data appears more hysteretic than they actually are. Some data points, which scattered in an irreproducible way, are regarded insignificant and not shown. Note that $T_N$ is highly reproducible, being free of sample- and field-dependences.
5 X-ray photoelectron spectroscopy (XPS) of AKD/CoO mixture

Table S1 Best-fitting parameters in XPS curve-fitting analysis

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$^a$ Fixed parameter $^b$ CoO 60vol% $^c$ CoO 40vol%
Figure S12. (a)-(i) Curve-fitting analysis of Co2p3/2 XPS of CoO with various fractal dimension $D$, and (j) $D$ vs relative intensity of peak components assumed at ~779, ~781 and ~782 eV. In (a)-(i) $D$ is shown in parentheses. Details of these results are summarized in Table S1.

6 Details of the calculation of $R_{S/C}$, $R_{S/V}$, and $R_{C/V}$

We assumed that CoO/AKD should consist of the solid figures shown in Figures S13(a)-(g). Each solid figure, in its turn, is comprised of identical cubes representing the CoO microparticles in the actual samples, and is different solely in their arrangements, which leads to different $D$s. Replacing the cubes by these solid figures, we obtain seven kinds of self-similar figures (“second generation”). By repeating the same procedure five times, we obtain seven kinds of more ideal fractal bodies with different $D$s (“fifth generation”). For example, the first three procedures for the solid figure in Figure S13(d) are progressively shown in Figures S14(a)-(c). We assumed such fractal bodies of the $n$-th generation as the model for the CoO/AKD system in this work because the diameter ratio between the typical CoO microparticle (= the cube) size and their aggregated structure (= the resultant fractal bodies) roughly corresponded to what was observed in their SEM. Thus the value of $n$ depended on the model, and it was selected so that the resultant fractal bodies was several hundred times as large as the cube. Then we calculated the resultant fractal bodies' surface areas, contact areas, and volumes.
Figure S13. Model solid figures as building blocks for fractal bodies used in calculation of surface areas, contact areas, and volumes. $D$s of resultant fractal bodies are (a) 3.00, (b) 2.93, (c) 2.87, (d) 2.73, (e) 2.50, (f) 2.25, and (g) 2.02, respectively.
Figure S14. Procedure for building fractal bodies in our model; (a) first generation, (b) second generation, and (c) third generation.
**Figure S15.** AC susceptibility of AKD/CoO mixture. No significant finite values were observed in imaginary part of AC susceptibility except for anomalies around $T_N$. 

7 Magnetic susceptibility of AKD/CoO mixture (2)
References


