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Pressure tuning of the exchange interactions between s-electrons in a b.c.c. lattice of sodalite cages

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Abstract

Néel (T_N) and Weiss (Θ) temperatures of the alkali-electro-sodalites (AES) loaded with Na or K were investigated as a function of hydrostatic pressure up to 2 GPa with a low-frequency ESR technique. T_N depends weakly on the pressure, but Θ decreases more sensitively with the pressure. The transfer energies t_1 and t_2 via the two-kinds of coupling windows, hexagons and squares, respectively, are derived with the tight-binding and the two-sublattice molecular field approximations. Assuming that the transfer energies are suppressed by the pressure exponentially, the observed pressure dependence of T_N and Θ can be reproduced very well and suggested that the electronic states in Na-ES can be scaled to that in K-ES with a chemical pressure of $\approx$ 4 GPa.

Key words: antiferromagnetism; sodalite; exchange interaction; hydrostatic pressure; electron spin resonance

Alkali-electrosodalite, $\mathrm{A_8(SiAlO_4)_6}$ (A is Na or K) is a prototypical compound suitable to study an effect of Coulomb correlation on the magnetism of the bcc electron lattice where each electron is trapped in a center of void called as β-cage and couples weakly through the hexagonal- and square-shaped windows as shown in Fig. 1. It has been reported that A-ES shows an s-electron antiferromagnetism below $\approx$ 50 K for Na-ES [1] and $\approx$ 80 K for K-ES [2]. In this report, we investigate the magnetism of A-ES by tuning the interaction between electrons with ESR under the hydrostatic pressure up to 2 GPa.

The Néel temperature, T_N has been demonstrated to be suppressed by pressure as shown in Fig. 2 [3,4]. Note that the T_N in Na-ES is suppressed more sensitively than in K-ES. With a naive expectation from a reduction of the lattice constant by pressure, it is expected for the electronic states to shift toward metal in a Mott-Hubbard phase diagram [5]. Since it is known that Na-ES and K-ES show insulating behavior with an energy gap [6], the observed suppression suggests a contrary tendency to the naive expectation. This is also suggested by the observation that the Weiss tempera-

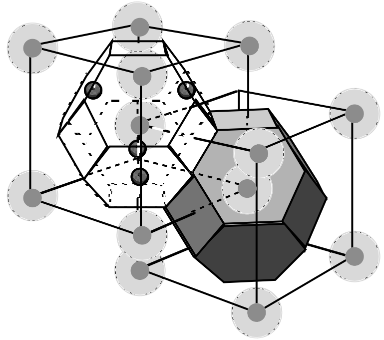

Fig. 1. A schematic structure of A-ES. The truncated octahedron represents Aluminosilicate cage, the small circles the alkali ions and the large circles the F-center electrons trapped in a square-well potential formed by four alkali ions. Oxygens locate on the each edge of the cage is omitted for brevity.

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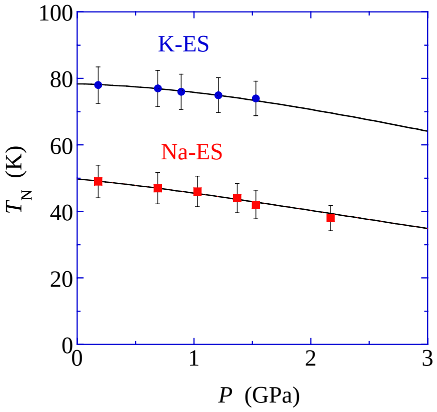

Fig. 2. The pressure dependence of the Néel temperature for Na-ES and K-ES. The solid curves represent the predictions deduced from the exponential dependence of the transfer energy in Eq. (3) which can successfully reproduce the data for both systems.

ture Θ suppressed with increasing pressure, as demonstrated for K-ES in Fig. 3.

The exchange energy J_1 and J_2 for the hexagonal and the square windows, respectivey, can be estimated with a relation predicted by the molecular field theory for two sublattices model, which is appropriate for the bcc electron lattice, as follows.

$$T_{\mathrm{N}} = \frac{2(z_1 J_1 - z_2 J_2)S(S+1)}{3k_{\mathrm{B}}} = \frac{(4J_1 - 3J_2)}{k_{\mathrm{B}}}, \qquad (1)$$

$$\Theta = \frac{(4J_1 + 3J_2)}{k_{\mathrm{B}}}, \qquad (2)$$

where z_1=8 and z_2=6 are the number of the nearest and the second nearest neighbor electrons, respectively. Further, the J's are transformed to the transfer energies t_1 and t_2 with a tight-binding relation, J_i=-4t_i^2/U. Thus obtained transfer enegy is found to follow an exponential pressure dependence,

$$t = t_0 \exp\left(-\frac{P}{P_0}\right), \qquad (3)$$

where P_0 is the characteristic pressure and t_0 is the transfer energy at ambient pressure. The parameters obtained by the fitting of eq. (3) to the data are shown in Table 1. The exponential dependence observed experimentally can be rationalized from the exponential dependence of the tunneling probability through the potential barriers caused by the negatively charged oxygens ions. Here, note that (1) t_2 between the second nearest neighbors is fairly close to t_1 between the nearest neighbors, especially in K-ES and (2) the characteristic pressure P_0 for t_1 is nearly twice of that for t_2, but depends only weakly on the species of alkali ions. This fact suggests that the electronoic states of A-ES are dominated mainly by the lattice constant and approxiamtely independent of the alkali ion species. Actually, it is suggested by the parameters in Table 1 that the difference of the electronic states in Na-ES from that in K-ES is attributable to the internal pressure of around 4 GPa.

Table 1
The parameters for the pressure dependence of the transfer energy t_1 and t_2 with the assumption of exponential dependence, $t(P) = t_0\exp(-P/P_0)$.

	t_0 (meV)		P_0 (GPa)	
	Na-ES	K-ES	Na-ES	K-ES
t_1	53	82	9.2	9.7
t_2	41	77	5.1	6.2

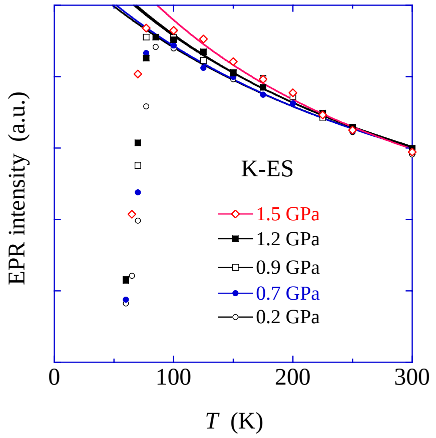

Fig. 3. The temperature dependence of the spin susceptibility in K-ES measured under hydrostatic pressures up to 1.5 GPa. The solid curves represent the Curie-Weiss law with the smaller Θ under the higher pressure.

In conclusion, the electronic states in Na-ES and K-ES are studied under the hydrostatic pressure. Both systems locate in the insulating side of the Mott-Hubbard phase diagram and are isostructural with internal pressure of 4 GPa on Na-ES. The pressure enhances the potential barriers between the electrons by closing the connecting windows.

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