Electronic states of alkali-electro-sodalite under pressure

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Abstract

Insulator-Metal transition of a bcc electron lattice in the alumino-silicate cage compound, $A_8(SiAlO_4)_6$, (A is Na or K) is investigated under high pressure. ESR has been measured to obtain the spin susceptibility that gives the Neel T_N and the Weiss Θ temperatures. They were analysed to give the exchange interactions J_1 and J_2 through the windows with a hexagonal and a square shapes. Finally, the transfer energies t_1 and t_2 through these windows were shown to follow exponential functions of the pressure with different characteristic pressures, giving rise to a comprehensive interpretation of the pressure dependence of T_N and Θ.

Keywords: Electron spin resonance, Metal-insulator phase transitions, Magnetic phase transitions

1. Introduction

Alkali-electrosodalite, $A_8(SiAlO_4)_6$ (A is Na or K) is a bcc lattice of F-center electrons trapped in a center of cavity named β-cage formed by aluminosilicate network. The electrons have s-like wavefunctions and couple weakly with each other through the hexagonal- and square-shaped windows as shown in Fig. 1. A-ES is known to have antiferromagnetic ground states of the s-electrons below ≈ 50 K for Na-ES [1] and ≈ 80 K for K-ES [2]. In this report, we study the magnetism of A-ES with ESR by tuning the interaction between electrons through the hydrostatic pressure up to 2 GPa. Fortunately, the aluminosilicate cage is relatively sensitive to the pressure because of the flexible O-M-O (M is Si or Al) bonding angle. The analysis of the Néel temperature T_N and the Weiss temperature Θ revealed that the exchange interaction between the second nearest neighbors plays important role for the antiferromagnetism in A-ES.

2. Experimental

Na- and K-doped sodalite were prepared with the reported methoed [3]. The spin susceptibility is measured with low frequncy ESR and NMR technique [4]. T_N is defined as a peak temperature of the ESR intensity in this report. Pressure is applied in a clamp type cell of Cu-Be with zirconia piston and daphne 7373 oil. Temperature dependence of the pressure is corrected, which is less than the error bar of the data.
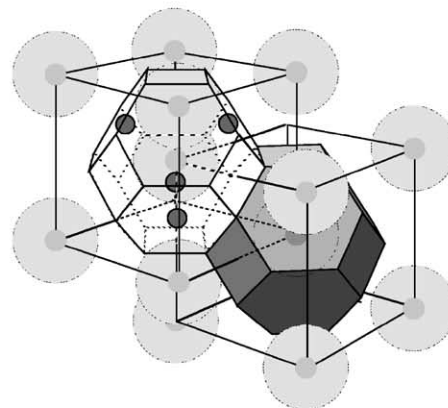
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Fig. 1 A schematic structure of A-ES. The truncated octahedron represents Aluminosilicate cage, the small circles the alkali ions and the large circles the F-center electrons trapped in a potential well formed by four alkali ions. Oxygens located on the each edge of the cage is omitted for brevity.

3. Results and Discussion

Figure 2 shows the temperature dependence of T_N for Na-ES and K-ES [5,6]. It is noted that the pressure change in T_N is as small as ~3 %/GPa in K-ES. There is, however, a strong contrast to that of Θ, where it is more than 20 %/GPa in Na-ES, as demonstrated in Fig. 3. There are two remarkable features in these Figures. The first is negative pressure coefficients in both T_N and Θ. The second is the above inconsistency between T_N and Θ. The first one could not be accounted for by a naive expectation for the effect on
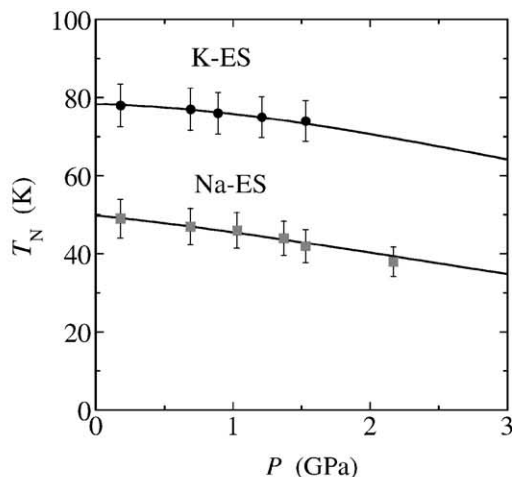
Fig. 2. The pressure dependence of the Néel temperature for Na-ES and K-ES. The solid curves represent the prediction of exponential dependence of the transfer integrals.
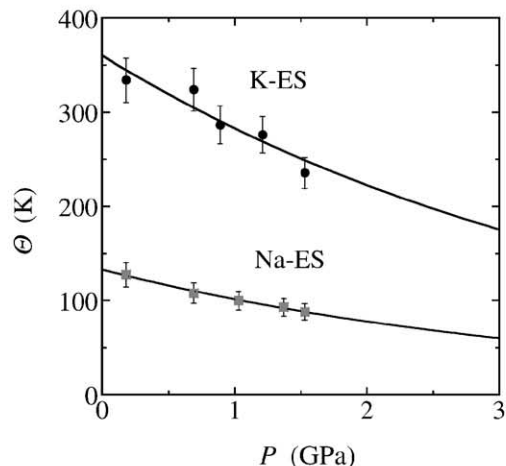

Fig. 3. The pressure dependence of the Weiss temperature in Na-ES and K-ES. The solid curves represent the prediction derived from the exponential pressure dependence of the transfer energy.

T_N and Θ by pressure that the reduced lattice constants makes Θ large, that is, Pauli-like. This fact suggests that the interactions between the electrons are suppressed by pressure, which can be interpreted by taking account of the effect on the β-cage. The flexible O-M-O bonding angle easily decreases with pressure, giving rise to closing of the coupling windows with the hexagonal and the square shapes that connect the nearest and the second nearest neighboring electrons, respectively. Therefore, the both systems are concluded to approach an insulating side of the Mott-Hubbard phase diagram [7].

The second point can be understood by the molecular field theory with a two sublattice model, appropriate for the bcc electron lattice. T_N and Θ are expressed by

$$T_N = \frac{2(z_1 J_1 - z_2 J_2) S(S+1)}{3 k_B} = \frac{4J_1 - 3J_2}{k_B} \quad (1)$$

$$\Theta = \frac{4J_1 + 3J_2}{k_B} \quad (2)$$

with the exchange energies J_1 and J_2, within a framework of the MF theory, where $z_1 = 8$ and $z_2 = 6$ are the number of the neighboring electrons. The suffixes 1 and 2 represent the nearest and the second nearest neighbors, respectively. Equations (1) and (2) explain why T_N and Θ behave differently from each other : the significant contribution of J_2. With Eqs. (1) and (2), one gets the pressure dependence of the exchange energies J_1 and J_2, It is surprisingly found that J_2 is comparable with J_1 at ambient pressure in K-ES, which is not considered in the reported calculations [8-10]. The transfer energies t_1 and t_2 can be estimated from J's with the tight-binding relation, $J = -4t^2/U$, where U is the on-site Coulomb repulsion energy. The solid curves in Figs. 2 and 3 represent the predictions of Eqs. (1) and (2) and the obtained transfer energies represented by an empirical formula of the exponential function as

$$t = t_0 \exp(-P/P_0), \quad (3)$$

where $P_0 \sim 9$ GPa for t_1 and ~ 5 GPa for t_2 are the characteristic pressures corresponding to a stiffness of the materials, independent of the alkali ion species, Na or K. This fact suggests that the electronic states of A-ES is governed by a size of the windows which is dominated by a size of the alkali ions. The larger the ionic size, the larger the window size to minimize the Coulomb repulsion among the alkali ions in a cage. Actually, the pressure dependence for Na-ES represented approximately by Eq. (3) can be scaled to that for K-ES with an internal pressure of ~ 4 GPa, arising from the smaller ionic size of 0.97 Å for Na$^+$ than 1.33 Å for K$^+$.

Finally, note that the prediction of Eqs. (1) and (2) with Eq. (3) is successful to reproduce both T_N and Θ excellently, which evidences the validity of the present analysis.

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