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Phase transition in alkali-electro-sodalite studied by ESR

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Abstract

AES (A= Na, K) is a Mott insulator at room temperature consisting of a bcc sub-lattice of F-centers, supported by a zeolite-like framework. Each sodalite cage contains an *s*-like electron trapped by a spherical potential due to four tetrahedrally arranged alkali cations. On cooling, SES and KES undergo an AF transition at about 50 and 70 K respectively, providing the first example of an *s*-electron antiferromagnet. ESR linewidth, lineshape and g-shift were measured, which shows unique feature of these *s*-electron lattices. The linewidth is narrow above T_N due to exchange narrowing and rapidly broadens below T_N. Under high pressures AES could be metal.

Keywords: Electron spin resonance, Magnetic phase transition,

Because of their structural simplicity and interesting electronic properties, the alkali-electro sodalites (AES, where A = Na, K, and Rb) are receiving an increasing attention. In Sodium Electro-Sodalite (SES), which consists of a zeolite-supported electron bcc lattice, electrons are separated by 6.9 Å. These electrons are associated with $\{4Na^+(e-)\}$ centers, similar to F centers in ionc solids. At ambient conditions SES is a Mott insulator, but acquires an antiferromagnetic ground state below 48 K.[1] SES is expected to undergo a Mott IM transition at higher pressures and we plan to use EPR spectroscopy to detect it. In preparation for this experiment we examined a high resolution EPR spectrum of SES at ambient pressure in order to learn about strength of the exchange interaction. We used a partially doped SES in which both exchange-coupled centers and those free of exchange interaction exist.

The EPR intensity of exchange-coupled centers has an anomaly at 50 K, as shown in Fig. 2. We find that SES is insulating above 50 K with EPR linewidth dominated by exchange-narrowed hyperfine structure due to $\{4Na^+(e-)\}$ centers. The estimated exchange energy at r.t. is -3.0 meV. This is consistent with J= -3.2 meV obtained from a mean-field relation with z=8 for bcc and Weiss temperature 150 K, as derived from the Curie-Weiss plot of EPR intensity. An abrupt increase of the resonance linewidth below 50 K is mainly due to decrease in the exchange frequency caused by antiferromagnetic ordering. The EPR signal at low temperatures comes from the relatively isolated electrons in the undoped part of the sample that remain paramagnetic below the T_c.

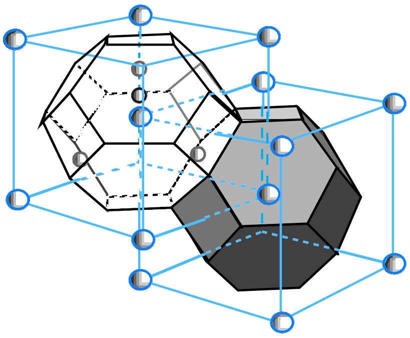

Fig.1 Schematic structure of SES. s-like electrons form a bcc lattice shown by the large balls. The small balls represent alkali atoms that surround an unpaired electron (the large balls). Sodalite cages are built of regularly alternating oxygen-sharing SiO_2 and AlO_2 units.

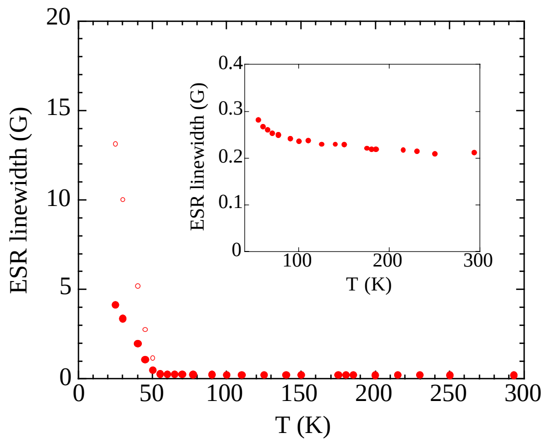

Fig.2 The peak to peak linewidth in SES taken at 1 GHz. Below 50 K the spectra are made of double Lorentzian. The open and closed circles represent a respective width. This can be attributed to a spread of exchange frequency that could be arose due to different numbers of nearest neighbour electrons. The inset is expanded view of the linewidth above 50 K.

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[1] V.I. Srdanov, G.D. Stucky, E. Lippmaa, and G. Engelhardt, Phys. Rev. Lett. **80** (1998) 2449, and references therein.