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Pressure (0–19 kbar) and temperature (4–300 K) dependent EPR study of Sodium-Electro-Sodalite (SES) is presented. SES, which consists of a bcc sub-lattice of F-centers supported by a zeolite-like framework, is known to be a Mott insulator at room temperature. On cooling, SES undergoes an AF transition at 48±2 K providing the first example of an *s*-electron antiferromagnet. We find that the width of the EPR resonance above T_N is influenced not only by a strong exchange interaction, but also by a fast spin-lattice relaxation. Also, with increasing pressure, T_N decreases linearly and extrapolates to 0 K at about 65 kbar. The reason for this seemingly unexpected behavior is briefly discussed.

Keywords: sodium-electro-sodalite; F-center; antiferromagnetic transition; EPR; line width; pressure

INTRODUCTION

Electronic properties of alkali-metal clusters in zeolites have attracted continuous interest. Recently, Nozue *et al.*[1] found a ferromagnetic behavior of unpaired *s*-like electrons in K-doped LTA, whereas Srdanov *et al.*[2] reported on an antiferromagnetic transition in SES. The unit cell formula of SES is $Na_8(AlSiO_4)_6$ and is obtained by inclusion of one sodium atom per cage of a salt-free sodium-sodalite, $Na_6(AlSiO_4)_6$. SES contains periodic array of F-centers consisting of an electron shared by four tetrahedrally arranged sodium cations. The unpaired electrons are arranged in a bcc sub-lattice, as shown schematically in Fig. 1. The nearest neighbor F-center electron wavefunctions do overlap, thus giving rise to a narrow impurity band within a 6 eV gap of the sodalite host[3,4]. No sign of a metallic behavior has been found in SES[2], suggesting strongly correlated electrons giving rise to a Mott-Hubbard insulator at

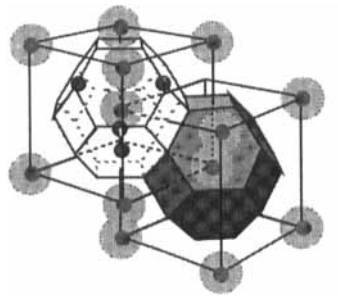

FIGURE 1 Schematic structure of SES. *s*-like electrons form a bcc lattice shown by the large spheres. The small balls represent alkali atoms that surround an unpaired electron (the large spheres). Sodalite cages are built of regularly alternating oxygen-sharing SiO_2 and AlO_2 units. Each corner of the truncated octahedron is occupied by Si or Al atom. Hexagons in this figure are actually flexible zigzag rings with additional six oxygen atoms. The bcc lattice constant is 8.881 Å for SES[2].

room temperature.

Here we report on a pressure and temperature dependent EPR study of the unpaired electrons in SES. Unlike majority of sodalites, SES cages do not contain central anion. Instead, the center of the SES cage is occupied by a single electron, making sodalite lattice more compressible. It is our assumption at this point that SES lattice contracts at even moderate pressures, in which case one should expect a change in SES electronic and magnetic properties. The change in the lattice parameters should affect electron density distribution, which in turn affects the magnitude of electron-lattice and electron-electron interaction. As a result one would expect change in the hyperfine coupling constants, electron spin-lattice relaxation rates, and exchange interaction. Consequently, change in the EPR line widths and the antiferromagnetic ordering temperature, T_N, should be observed. Indeed, these changes have been detected experimentally. The slight change in the EPR line widths were analyzed in the spirit of the exchange narrowing theory of Anderson and Weiss[5], and compared with experiment. The excessive line width of the EPR signal has been linked to the spin-orbit interaction causing a rapid electron-lattice relaxation. Also offered is an explanation for the negative slope observed in the $\partial T_N/\partial P$ measurements.

EXPERIMENTAL

The salt-free sodium-sodalite[6] was used to obtain SES by Na vapor doping[7].

The temperature dependent EPR study was conducted on a home built EPR spectrometer, capable of changing both probe frequency and pressure. The EPR of SES was studied at low frequencies, down to 30 MHz, and temperatures between 4.2 and 300 K[8,9]. Hydrostatic pressure of up to 19 kbar was applied by using a clump type cell made of BeCu filled with Daphne 7373 oil as a pressure medium. The pressure drop due to oil contraction at lower temperatures has been accounted for by using experimental data of Murata[10].

RESULTS AND DISCUSSION

EPR line width at ambient pressure

The temperature dependence of EPR peak-to-peak line widths at ambient pressure is shown in Fig. 2. On cooling down to 50 K, the EPR line width increases somewhat but remains below 1 G. The resonance line-shape is well reproduced by two Lorentzian functions, suggesting that the observed spectra are exchange narrowed. This is consistent with the large Curie-Weiss constant ($\Theta \approx -200$ K) and the Néel temperature of $T_N = 48$ K. The correlation between EPR line width and the strength of the exchange interaction can be examined more quantitatively by comparing theory[5] with the calculated second moments of the local fields produced by electron-dipole and hyperfine interactions.

According to Anderson and Weiss[5] the EPR half width at half amplitude,

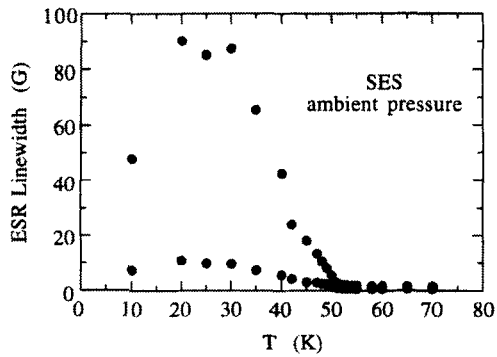

FIGURE 2 The peak to peak EPR line width in SES taken at 45 MHz. Below 50 K the spectra are made of double Lorentzian. The steep increase of line width below 50 K is an indication of antiferromagnetic ordering. In addition to this broadening, the integrated intensity rapidly decreases as shown in Fig. 3.

TABLE I Several parameters for the exchange narrowing of EPR

$(10/3)\langle(\Delta H^2)\rangle_{dip}$ (G^2)	$\langle(\Delta H^2)\rangle_{hf}$ (G^2)	ω_{ex}/γ_e (G)	ΔH_{cal} (G)
3.0×10^4	5.5×10^3	7.2×10^5	0.05

ΔH, narrowed by the exchange coupling $-JS\bullet S$ can be expressed as

$$\Delta H_{cal} \approx \gamma_e\langle(\Delta H^2)\rangle/\omega_{ex}, \tag{1}$$

where $\langle(\Delta H^2)\rangle$ is the total second moment[11], $\omega_{ex}=J/\hbar$ is the exchange frequency, and $\gamma_e=1.76\times10^7$ G^{-1}s^{-1} is the gyromagnetic ratio for the electron. Major parts of the second moment are due to the electron dipole interaction and the hyperfine contact interaction between the unpaired electron and four ^{23}Na (I=3/2) nuclei. These estimates are given in Table I, assuming point dipole spins located at the center of cages and the hyperfine coupling constant for ^{23}Na in SES to be on the order of 33 G. The latter was extracted from the hyperfine split EPR spectra in a partially doped SES, observable only at 4.2 K[12] and is slightly larger than 31 G in sodium-chloro-sodalite (SCS)[13]. Since the lattice constant is nearly identical in the two sodalites[14], this difference implies an effect of the additional attractive potential of Chlorine atom in SCS. Note that the characteristic 13 peak EPR hyperfine pattern of Na_4^{3+} clusters is absent in the present SES due to exchange narrowing. The dipolar contribution to the total line width was obtained by multiplying diagonal term by factor 10/3 in order to account for the off-diagonal term[5,11]. The exchange field, ω_{ex}/γ_e was derived following reference [5] and using experimentally determined Curie-Weiss temperature, $\Theta\approx$ -200 K[2]. We note that the calculated EPR line width of ΔH_{cal}=0.05 G is an order of magnitude smaller than the experimental one. The apparent inconsistency has been removed by power saturation measurements at 40 MHz, showing that the EPR line width in SES is dominated by the fast spin-lattice relaxation rate, $T_1^{-1}\approx10^7$ s^{-1}. There are two possible mechanisms to account for this fast electron spin-lattice relaxation rate: thermal modulation of the dipolar and hyperfine fields[15] and/or the spin-orbit interaction. The former is a typical mechanism in insulators, but usually it is too small to explain the observed relaxation rate. Therefore, the latter is more likely to be the case and is supported by preliminary EPR data on potassium-electro-sodalite (PES). The EPR line width of PES is twice that in SES, yet the spin ordering temperature in PES (T_N = 72 K)[16] is higher than in SES, thus implying

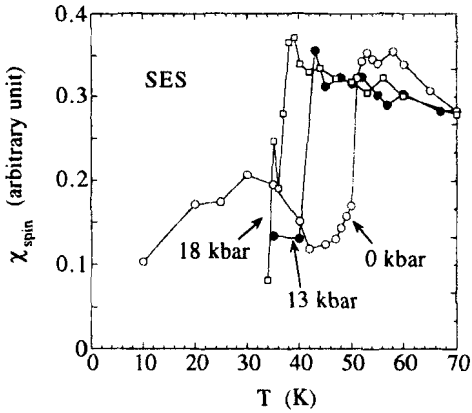

FIGURE 3 The temperature dependence of EPR integrated intensity of SES taken around 40 MHz under three different pressures; ambient, 13 and 18 kbar estimated around these temperature range, by subtracting 1.5 kbar from the nominal pressure at 300 K, P_{300K}. Find a clear decrease of the antiferromagnetic transition temperature.

a stronger electron exchange interaction in PES.

Pressure dependent EPR measurements

Figures 3 and 4 demonstrates how T_N changes with the applied pressure. The initial motivation for pressure-dependent studies of electro-sodalites was to induce the Mott metal-to-insulator transition at higher pressures. Instead, as shown in Fig. 4, we find that the Néel temperature, T_N, in SES decreases linearly with the applied pressure. This may seem surprising in the view that the electron-electron separation in compressed SES must be reduced so that better

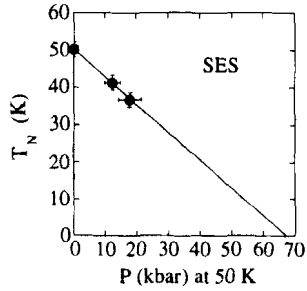

FIGURE 4 Pressure dependence of T_N, which predicts T_N goes to 0 K at about 65 kbar, that is, the electrons are localized each other.

overlap of the electron wavefunctions is to be expected. On the other hand, shrinking of the sodalite lattice pushes oxygen atoms towards the center of the twelve (hexagons) member rings, which is accomplished by reducing the T-O-T angle (T = Al or Si) while maintaining the Si-O and Al-O distances unchanged. This makes Na_4^{3+} center smaller which deepens the potential well for trapped electron. As a consequence, the effective F-electron radius decreases so does the overlap integral between neighboring centers.

Figure 4 also indicates that the simple extrapolation of T_N reaches 0 K at 65 kbar. Since the exchange interaction goes to zero at this pressure, we would expect that EPR spectrum loses the exchange narrowing effect, and finally typical 13 peaks due to hyperfine interaction with four Na nuclei would reappear.

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