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Magnetism of F centers; indication of an antiferromagnetic phase transition in potassium-electro-sodalite*

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Temperature-dependent EPR data of potassium-electro-sodalite (PES), $K_8[Al_6Si_6O_{24}](e^-)_2$, are consistent with the occurrence of an antiferromagnetic phase transition at 71±2 K. PES is a Mott insulator which contains an unpaired electron in every sodalite cage. The same transition in sodium-electro-sodalite occurs at a considerably lower temperature (42 K), indicating that the exchange interaction among localized electrons is stronger in PES. PES is obtained by the inclusion of one potassium atom in every cage of potassium sodalite. The ^{27}Al MAS NMR resonance of PES is shifted downfield in respect to diamagnetic potassium-sodalite, $K_6[Al_6Si_6O_{24}]$. The NMR shift is due to unpaired electrons and is caused by hyperfine Fermi contact interaction.

Keywords: sodalite, F center, AF transition.

INTRODUCTION

A color center (also known as F center) in ionic solids consists of an unpaired s-like electron localized in the spherical cavity of a missing halogen anion. These centers are normally present in ppm quantities, randomly distributed throughout the entire solid. Due to the ionic nature of the host, the size of the F center electron wavefunction is much smaller than the average distance between F centers. As a consequence, no magnetic interactions between the unpaired electrons associated with such F centers are possible.

As discovered by Rabo,[1] much higher F center densities are attainable in alkali metal doped zeolites. Because of their structural complexity, zeolites can host a variety of different paramagnetic centers making their magnetic studies difficult to interpret. This is not the case with sodalite where only one type of F centers can occur. In sodium-electro-sodalite the F center consists of one electron shared by four equivalent sodium cations, $[4Na^+ (e^-)]$, better known as Na_4^{3+} cluster.[2,3] Recently, an antiferromagnetic phase transition was found at 48 K in sodium-electro-sodalite

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[*] Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday.

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(SES), an unusual sodalite which represents the first ordered cubic lattice of such centers.[4] In this article, preliminary data on the potassium analogue of SES, the potassium-electro-sodalite, abbreviated hereafter as PES, are presented.

EXPERIMENTAL

We took advantage of the ion-exchange properties of sodalites to first synthesize potassium-sodalite which was used as a precursor for PES. Starting with hydrothermally synthesized sodium-hydroxyl-sodalite hydrate, the NaOH unit was extracted from every cage to obtain sodium-sodalite hydrate: $Na_8[Al_6Si_6O_{24}](OH)_2{\cdot}2H_2O - 2NaOH + 6\ H_2O = Na_6[Al_6Si_6O_{24}]{\cdot}8H_2O$. The latter was transformed into $K_6[Al_6Si_6O_{24}]{\cdot}nH_2O$[5] by ion exchange reaction, and subsequently converted into $K_6[Al_6Si_6O_{24}]$ by heating the sample at 400 ºC under vacuum. The final product, PES, was obtained by exposing $K_6[Al_6Si_6O_{24}]$ sodalite to potassium vapor for 48 hours at 300 ºC, in an evacuated pyrex tube. PES forms by inclusion of one potassium atom per cage of dehydrated potassium-sodalite: $K_6[Al_6Si_6O_{24}] + 2K = K_8[Al_6Si_6O_{24}]$. Note that the sodalite unit cell contains two cages. The PES samples were characterized by powder X-ray diffraction, as well as EPR, and NMR spectroscopy. The following instrumentation was used: Scintag PAD diffractometer equipped with a hermetically closed beryllium cell, General Electric GN-300 NMR spectrometer with a MAS probe, and a Bruker EPR spectrometer equipped with an Oxford 9100 liquid-helium flow-cryostat.

RESULTS AND DISCUSSION

Like in any other sodalite, the PES framework consists of regularly alternating oxygen-sharing AlO_4 and SiO_4 tetrahedra with Si and Al atoms occupying the apexes of the truncated octahedron. Inside every PES cage there are four potassium ions surrounding an electron. When the PES unit cell formula, $K_8[Al_6Si_6O_{24}](e^-)_2$, is compared with that of an anion-bearing sodalite, $K_8[Al_6Si_6O_{24}]Br_2$, it becomes clear that the halogen anion in every sodalite cage is replaced by an unpaired electron in PES. Such a substitution has a profound impact on the physical properties of the solid because it transforms a diamagnetic insulator into a Mott insulator with a large unpaired electron spin density ($2.53{\times}10^{21}$ cm^{-3} in case of PES). While its precursor is a white, PES is black with some blue overtones. The PES lattice is cubic, space group P-43n and $a_0 = 9.245(5)$Å.

In PES all the aluminium atoms are equivalent, which is consistent with the single ^{27}Al MAS NMR resonance found at 81 ppm (Fig. 1). The downfield shift of about 40 ppm with respect to the resonance of the diamagnetic KES procursor is mainly due to the presence of unpaired electrons. The shift is known as a paramagnetic shift and is caused by Fermi contact interaction between unpaired electrons and Al nuclei. A small portion of the shift is due to the slightly different Al–O–Si bond angles in the two sodalites, causing a small chemical shift in the same direction. If exposed to air, a new resonance at 54 ppm appears in the ^{27}Al NMR spectrum of PES (see Fig. 1b). The resonance originates from aluminium atoms in the sodalite cages near the crystalline surface which were penetrated by oxygen. The ralative ratio of the two peaks suggests that about 30 % of the F centers are destroyed upon exposure to air. Nevertheless, once the damage has occurred, the rest of the cages appear to be protected indefinitely.

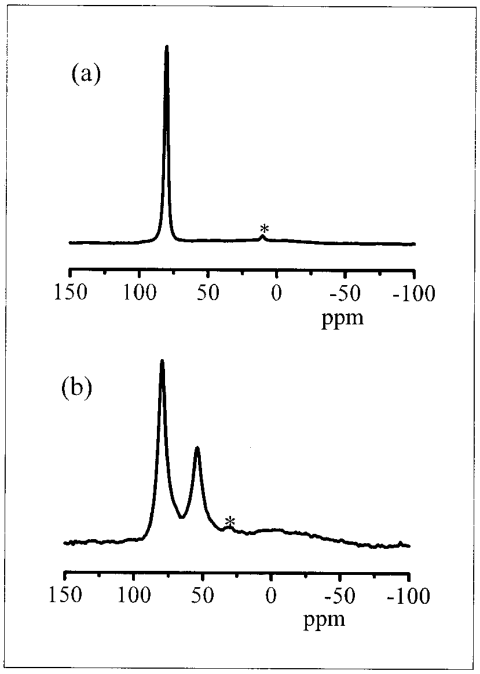

Fig. 1. The ^{27}Al MAS NMR spectra of PES (a) before exposure to air; (b) after exposure to air for 24 h; (* - spinning side bands).

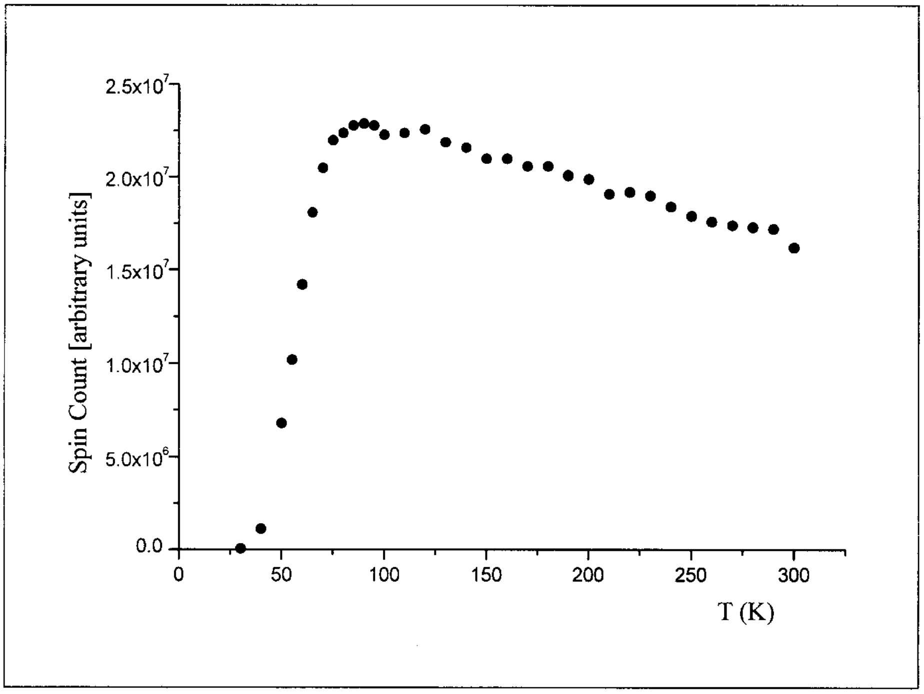

Fig. 2. Temperature-dependent EPR data of PES.

The PES NMR data show that a significant portion of the F-center electron density is at the cage walls so that wavefunction overlap (hence the exchange interaction) between electrons in neighboring cages may be expected. Indeed, the EPR signal of [4K+ (e^-)] centers in PES has no hyperfine structure which is the consequence of exchange narrowing. The exchanged-narrowed EPR resonance of PES occurs at g = 1.998(5) and has a half-width of about 1.3 G. On cooling, the integrated intensity of the EPR signal increases slightly until about 80 K at which temperature, as shown in Fig. 2, a rapid decrease of the signal intensity commences. Such a behavior is consistent with an antiferromagnetic phase transition which was also detected in SES at 48 K.[4] The Neel temperature in PES estimated from the EPR data in Fig. 2 is about 72 K. The higher Neel temperature in PES than in SES implies better wavefunction overlap, which may seem surprising considering larger separation of the unpaired electrons in PES. The most likely reason is that the Coulomb attraction of the alkali ions and the electron is stronger in the [$4Na^+(e^-)$] than in the [$4K^+$ (e^-)] center thus allowing for a larger spatial volume of the electron wavefunction in PES.

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ИЗВОД

МАГНЕТИЗАМ Ф ЦЕНТАРА: ИНДИКАЦИЈА АНТИФЕРОМАГНЕТНОГ ФАЗНОГ ПРЕЛАЗА КОД КАЛУЈУМ-ЕЛЕКТРО-СОДАЛИТА

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Температурска зависност EPR сигнала калијум-електро-содалита (PES), $K_8[Al_6Si_6O_{24}](e^-)_2$, указује на постојање антиферомагнетне фазне трансформације на 71±2 K. PES је Mott-ов изолатор који садржи по један неспарен електрон у сваком содалитском кавезу. Иста фазна трансформација дешава се код натријум-електро-содалита на знатно нижој температури (42 K), указујући да је интеракција измене између локализованих електрона јача код PES-а. PES је добијен инклузијом по једног атома калијума у сваки кавез калијум-содалита. ^{27}Al MAS NMR резонанца PES-а је померена ка већим вредностима ppm-а у односу на дијамагнетни калијум-содалит, $K_6[Al_6Si_6O_{24}]$. Ово NMR померање потиче од неспарених електрона и условљен је хиперфином Fermi-контакт интеракцијом.

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