PHYSICAL REVIEW B VOLUME 44, NUMBER 6 1 AUGUST 1991-II

Conduction-electron spin resonance of Na-Cs alloys in zeolite *Y*

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(Received 11 March 1991)

The *g* shift of the conduction-electron spin resonance of Na-Cs alloy clusters is zeolite Na*Y* has been measured and is found to follow the simple Elliot relation. In this model, the *g* shift depends upon the ratio of the spin-orbit coupling and energy-band separation. The assumption of a linear variation of both these parameters across the alloy series gives rise to a nonlinear variation of the *g* shift, as is found experimentally. The spin susceptibility changes from a Curie to a Curie-Weiss law with increasing Cs content, contrary to the predictions of the quantum size effect for noninteracting particles.

The shift of the conduction-electron spin resonance (CESR) from the free-electron *g* value has been shown to be related to the atomic spin-orbit coupling, λ. Using a perturbation technique, Elliot[1] showed that

$$\Delta g \cong \lambda / \Delta E \ , \qquad (1)$$

where Δg is the difference between the CESR and the free-electron *g* values, and ΔE is the energy difference between the conduction band and the next band with the appropriate symmetry. On the basis of Eq. (1), the *g* shift of the CESR should become larger with increasing spin-orbit coupling down any series of simple metals. This has been demonstrated for the alkali metals, using bulk crystals, small particles, and metallic clusters in zeolites.[2]

The open arrangement of cavities and connecting apertures has made the zeolites ideal hosts for preparing dispersed metallic clusters.[3] A general chemical formula for the zeolite family is $M_x[(\mathrm{AlO_2})_x(\mathrm{SiO_2})_y]\cdot z\mathrm{H_2O}$, where the tetrahedrally coordinated Al^{3+} and Si^{4+} are linked by corner sharing of O^{2-} ions to form an anionic lattice. Charge-compensating cations, usually Na^+, are located at particular cationic sites[4] within the three different types of cavity. Zeolite NA*Y*, synthesized from analytical grade pure chemicals, was used for the ion-exchange procedures to obtain new zeolites with mixed cationic contents.[5] The formula of the unit cell of Na*Y* is $\mathrm{Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]}\cdot z\mathrm{H_2O}$, where only the 40 Na^+ ions in the so-called large α cages can be exchanged with the larger Cs^+ ions. The remaining 16 Na^+ ions are located in other, smaller cavities, which cannot be permeated by Cs^+ ions. The alloys studied here were therefore formed only between the exchangeable cations in the α cage. To prepare one particular alloy, the necessary stoichiometric amount of CsCl (e.g., 594 mg CsCl, Merck, suprapur) was added to a suspension of 3.0 g dehydrated zeolite Na*Y* in 1 l distilled water and was stirred overnight at 80 °C, then filtered, washed with distilled water, and dried in air. This amount of CsCl produced a sample with an ion mole fraction $x_{\mathrm{Cs}^+}=n_{\mathrm{Cs}^+}/(n_{\mathrm{Cs}^+}+m_{\mathrm{Na}^+})=0.375$, for the alkali metal ions located in the largest α cages. 1.0 g of this ion-exchanged $[\mathrm{Cs}_n\mathrm{Na}_m Y]$ was then dehydrated at 450 °C in a vacuum system and pumped overnight in a Pyrex$^{\mathrm{TM}}$ apparatus, which also contained 80 mg pure caesium in a thin Pyrex capsule. The caesium was distilled into the system after breaking the capsule with an iron bar actuated by an external magnet. The zeolite sorbs the distilled metal from both the vapor and liquid phases at room temperature. During the very slow sorption from the vapor phase, which always precedes the rapid sorption from the liquid phase, a red coloration is observed, indicating the formation of stable $\mathrm{Na_4}^{3+}$ clusters. The addition of 80 mg Cs to the exchanged zeolite corresponds to the inclusion of a further 8 atoms per unit cell, which are not only capable of reducing the alloyed ions already present owing to the ion exchange process but also of being included into the alloy. The new mole fraction, including the sorbed Cs atoms, is now $x_{\mathrm{Cs}}=0.48$ for this particular example and this value is the one used for our data analysis. Samples with different molar fractions of total Cs content were prepared by ion exchange with different amounts of CsCl.

The electron spin resonance spectra were taken with a Bruker ER 200 D-SRC *X* - band spectrometer, with the samples cooled in an Oxford Instruments ESR-900 gas flow cryostat. After adsorption of caesium metal onto the zeolite from the liquid phase at room temperature, the samples near the middle of the alloy spectrum showed a split spectrum as expected from a two-phase material, but this could be converted into a single Lorentzian by annealing for 2 days at 120–150 °C. Lorentzian line shapes are expected as the metallic particle sizes are less then the penetration depth. An example of the ESR

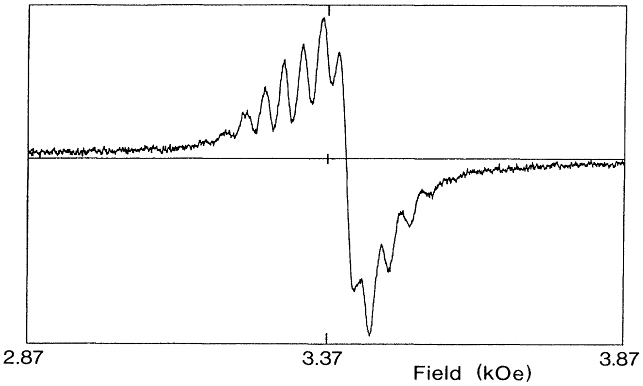

FIG. 1. ESR spectrum of the Na_4^{3+} cluster and a particular Na-Cs alloy with a mole fraction of $x_{Cs}=0.48$. The metallic ESR signal is shifted to higher field, as seen in the unequal distribution of the Na_4^{3+} absorption lines on both sides of the metallic signal. The microwave frequency was 9.43 GHz and the temperature 4.4 K.

spectrum of a single-phase material after reduction is shown in Fig. 1, which shows a 13-line hyperfine split spectrum superimposed on a Lorentzian due to the alloy clusters. While it is possible to saturate the 13-line signal, the Lorentzian does not saturate up to 100 mW of microwave power as is usually found for CESR of metals. Furthermore, it was noted that changing the alloy concentration leaves the 13-line spectrum at the same field, while the Lorentzian moves to a higher field with increasing Cs content. The 13-line spectrum is due to the well-known Na_4^{3+} centers[2,6,7] located in the smaller β cages and are formed by transfer of an electron from alloyed caesium atoms in the α cage to the four sodium ions in the β cage, which do not form an alloy with the caesium, as already mentioned. These centers are also the source of the red coloration during the Cs absorption. The broad Lorentzian line of Fig. 1 is assigned to the reduced alloy clusters and the variation of its g value with the Na mole fraction is shown in Fig. 2. At high sodium concentration, the g value is constant, followed by a nonlinear decrease to the pure Cs value. Electrons are freed by the additional 8 Cs atoms per unit cell absorbed by the zeolite containing the alloy clusters as well as the Na_4^{4+} in the smaller cavities. These electrons give rise to the ESR signal and are distributed over both kinds of clusters, with a preference for the Na_4^{4+} clusters in those zeolites with a high sodium concentration, thus converting them to paramagnetic Na_4^{3+} centers. Hence, the concentration-independent Na g value observed over the first 0.22 mol fraction of Cs in Na*Y* in Fig. 2 is due to this preference.

The variation of the g value over the rest of the alloy system in Fig. 2 may be explained using Eq. (1) and a rigid band model, which assumes λ and ΔE are atomic averages and vary linearly with composition. Let λ_1 and ΔE_1 be the parameters for Cs and λ_2 and ΔE_2 those for Na. Then for an alloy with x mole fraction of Na

$$\lambda=\lambda_1(1-x)+x\lambda_2=\lambda_1+x(\lambda_2-\lambda_1) \tag{2}$$

and

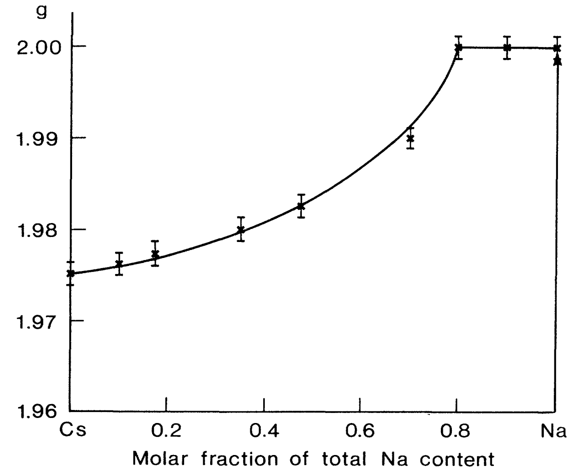

FIG. 2. The calculated g shift (solid line, calculated from Eq. (4)) compared with the experimental values (crosses). The mole fraction of Cs is calculated as a fraction of the total cation concentration including the 8 adsorbed Cs mol per unit cell used in the reduction process.

$$\begin{aligned}\Delta E&=\Delta E_1(1-x)+x\Delta E_2\\&=\Delta E_1+x(\Delta E_2-\Delta E_1)\end{aligned} \tag{3}$$

which, when substituted into Eq. (1), give an expression for the g shift in terms of four parameters. This may be reduced to a three-parameter expression by taking the slope m_1 near $x=0$ and m_2 near $x=0.78$, from which it may be shown that the g shift of an alloy, Δg, is given by

$$\Delta g=\Delta g_1\frac{1+x\left[\frac{\Delta g_2}{\Delta g_1}\left[\frac{m_1}{m_2}\right]^{0.5}-1\right]}{1+x\left[\left[\frac{m_1}{m_2}\right]^{0.5}-1\right]}\;, \tag{4}$$

where Δg_1 and Δg_2 are the g shifts of Cs and Na, respectively. The curved line in Fig. 2 is a fit to Eq. (4), showing good agreement between the rigid band model and the experimental points over the concentration range 0–0.78 mole fraction of Na.

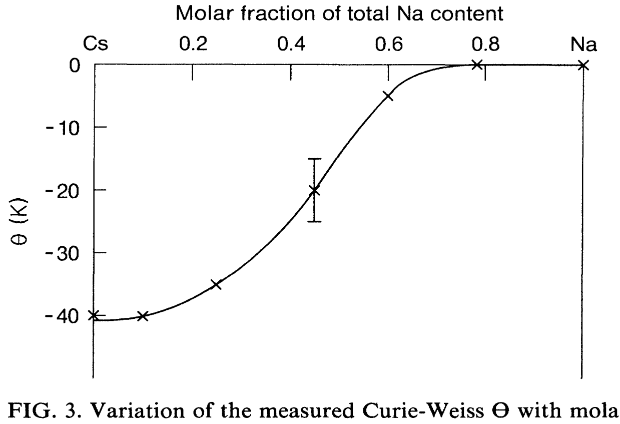

FIG. 3. Variation of the measured Curie-Weiss Θ with molar fraction of total Cs content.

A measure of the spin susceptibility of the alloys was obtained by comparing the CESR signal intensity with that of a known ZnS:Mn powder paramagnet. The temperature dependence of this spin susceptibility follows a Curie law for samples containing metallic Na clusters, but a Curie-Weiss law for two different samples containing pure Cs clusters with $\Theta = -40 \pm 5$ K. Measurements on some of the samples used to obtain Fig. 2 show that the Curie-Weiss Θ varies in a somewhat similar manner with alloy composition as the g value. This variation, shown in Fig. 3, suggests it is an intrinsic effect of these small alloy clusters. The quantum size effect[8] predicts a Curie law for odd-numbered clusters as small as these if they are isolated, as the electron energy level separation becomes larger than kT and the uppermost occupied level contains a single unpaired electron. This is found for the Na clusters but as an increasing amount of Cs is added to the clusters deviations from the Curie law are apparent. Such deviations from the predictions of the quantum size effect across the alloy system may be due to interaction between the clusters as the smaller Na atoms are replaced by larger Cs atoms in the cavities. Clusters containing the larger atoms will more completely fill the cavity and may interact with the clusters in the neighboring cavities through the connecting apertures of the zeolite lattice. The interaction will reduce the electron-level spacing of the now imperfectly isolated clusters and may also be antiferromagnetic in nature which will also give rise to a Curie-Weiss susceptibility with negative values of Θ. An antiferromagnetic interaction is to be expected simply from the electron transfer between particles with a single unpaired electron where the transferred electron will enter its neighbor with antiparallel spin. The lower work function of Cs should assist the electron transfer in the Cs-rich alloys making the effect more apparent at the Cs end of the alloy spectrum.

The authors thank Professor K. A. Müller and Professor E. Schumacher for many stimulating discussions. F. Blatter also thanks the Swiss National Foundation, Grant No. 20-25325.88, and the "Kommission zur Förderung der wissenschaftlichen Forschung, Jucker/Sieber," Grant No. (1467)1211, for financial support.

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