Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974, and Ames Laboratory, DOE, and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Properties of Sc_7Cl_{10} Revisited

F. J. DiSalvo,*† J. V. Waszczak,† W. M. Walsh, Jr.,† L. W. Rupp, Jr.,† and John D. Corbett‡

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The properties of the pseudo-one-dimensional compound Sc_7Cl_{10} have been reinvestigated down to 4.2 K. Sc_7Cl_{10} is a good conductor and has local magnetic moments (0.90 μB/formula unit). The EPR spectrum shows a line without hyperfine structure with a g value of 1.985. The lack of hyperfine structure suggests rapid spin diffusion, possibly as a result of the metallic conduction inferred from resistance and photoemission data. The observed g value and the moment determined from magnetic susceptibility indicate about one localized magnetic moment per 2 formula units, an assignment that is inconsistent with the room-temperature structure of Sc_7Cl_{10} and simple magnetic models.

Introduction

The reduced scandium halide Sc_7Cl_{10} has a structure containing double octahedra of Sc atoms that share edges to produce infinite chains.[1] These chains are surrounded by the chlorine atoms. A second chain made from single Sc atoms centered in chlorine octahedra sharing edges separates the larger double-octahedral metal chains and further lessens the coupling between the double chains (see Figure 1). Since the scandium is only partly reduced (+1.43) and since the structure has strong one-dimensional characteristics, we thought it possible that Sc_7Cl_{10} could show phase transitions similar to those seen in many other quasi-one-dimensional systems such as $NbSe_3$.[2] While we have not found such phase transitions in Sc_7Cl_{10}, we have extended the measurement of properties down to 4.2 K and consequently have modified an earlier interpretation of the previously measured properties of Sc_7Cl_{10}.[1]

Experimental Section

Synthesis. The samples of Sc_7Cl_{10} were prepared in good yields at Ames Laboratory by the method previously described.[1] Since the material is air-sensitive, all handling for synthesis and for measurement was carried out under drybox atmospheres.

Magnetic Susceptibility. Polycrystalline samples were sealed in high-purity fused-silica tubes under a helium atmosphere, and the susceptibility was measured down to 4.2 K by the Faraday method with a previously described apparatus.[3] The absolute accuracy of the susceptibility determined by several standards is 2%,[3] while the relative accuracy is better than 0.1%.

Electrical Conductivity. The resistance of a small pellet of polycrystalline Sc_7Cl_{10} compacted by using stainless-steel pistons under a force of approximately 100 lbs was measured at room temperature in an Al_2O_3 tube (i.d. = 0.125 in.).

Electron Paramagnetic Resonance. The EPR spectra were obtained at room temperature and 150, 77, 4.2, and 1.6 K for a polycrystalline sample that had been embedded in silicone grease in the drybox. The spectra were obtained with a conventional homodyne bridge operating at 12 GHz. Field modulation at 165 Hz with lock-in detection yields magnetic field derivative spectra.

Results

The magnetic susceptibility from 200 to 4.2 K is shown in Figure 2. The data could be least-squares fit over the entire temperature interval by the Curie–Weiss expression: $\chi_g = C_g/(T - \Theta) + \chi_0$,[4] where C_g is the Curie constant, Θ is the temperature of interaction between the magnetic moments, and χ_0 is a temperature-independent term. The result of the fit is $C_g = 15 \times 10^{-4}$ (emu K)/g, $\Theta = -1.4$ K, and $\chi_0 = 0.45 \times 10^{-6}$ emu/g with a least-squares error of 0.7% for 150 data points. The data at temperatures greater than 77 K fall within the error bars given for the previous measurement.[1]

The electrical resistance of a polycrystalline pellet of Sc_7Cl_{10} with a diameter of 0.125 in. and a length of 0.2 in. was about 1 Ω along the cylinder axis. No estimation of the interparticle contact resistance could be made, so we can only put an upper limit on the electrical resistivity of Sc_7Cl_{10} at room temperature of $\rho < 5 \times 10^{-2}$ Ω cm. This value would be an upper limit for the average resistivity. The resistivity is expected to be anisotropic in a material with strongly one-dimensional structural characteristics, being lowest along the chain direction. Anisotropies as large as 10^2 are observed in other quasi-one-dimensional-systems.[5] So it seems likely that the conductivity along the Sc chains is large and metallic.

A single EPR line was observed at all temperatures, and a strong microwave loss typical of a metallic sample was apparent. At room temperature the line width and position ($\Delta H = 54$ G, $g = 1.985$) agreed quite well with the original observation of ref 1. On cooling, significant narrowing occurred to 77 K ($\Delta H = 20$ G) followed by some broadening at 4.2 K ($\Delta H = 40$ G). At the lowest temperature the line broadened markedly on its low-field side, and the signal intensity ceased to increase as T^{-1} as it had at the higher temperatures. Such behavior suggests antiferomagnetic ordering would occur at a somewhat lower temperature, as is also suggested by the small Θ value obtained in the susceptibility measurement.

No other resonance could be detected over the entire 24-kG range of the magnet, equivalent to the interval $0.36 < g < \infty$. The search was carefully made in hopes of detecting a weak, temperature-idependent resonance corresponding to the Pauli paramagnetism of the mobile carriers. These carriers produced strong microwave electrical loss supporting the suggestion of metalic conductivity mentioned above.

Discussion

The electrical measurements, along with the UV[6] and X-ray[7] photoemission spectra suggest that Sc_7Cl_{10} is metallic or at least a small bandgap semiconductor ($\lesssim 0.3$ eV). The positive value of χ_0 obtained from the magnetic measurements is also consistent with the above observation. χ_0 is due to the sum of three terms: the core diamagnetism, the Pauli–Landau paramagnetism originating with the conduction electrons in a metal, and the Van Vleck paramagnetism due to second-order coupling of the occupied d levels to the unoccupied d levels by the applied magnetic field.[8] In Sc_7Cl_{10} the paramagnetic effects outweigh the diamagnetic core contribution; however, from susceptibility measurements alone the two paramagnetic contributions cannot be separated. Note that the previous interpretation of the magnetic properties[1] was

† AT&T Bell Laboratories.
‡ Iowa State University.

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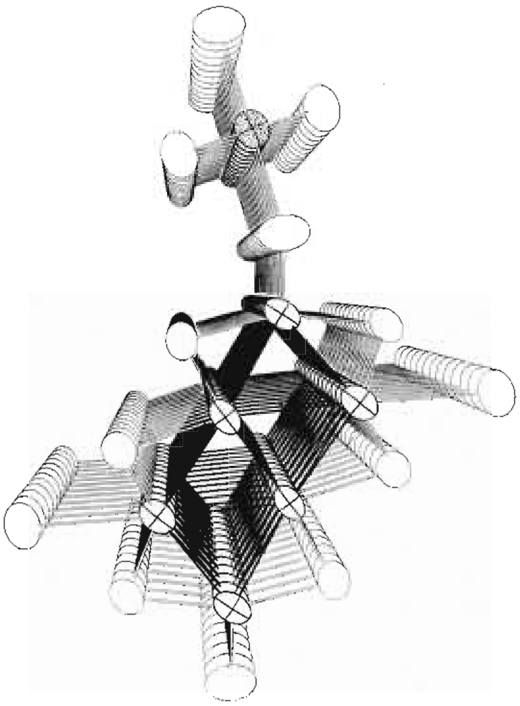

Figure 1. View of the structure of Sc_7Cl_{10} almost along the chain axis. The 90% probability thermal ellipsoids are given for each atom: those for chlorine are open, those for the Sc atoms in the double chain of octahedra are crossed, and the Sc atoms in the single chain within chlorine octahedra are dappled (and crossed). These units are further interconnected by chloride bridging between different types of scandium chains.

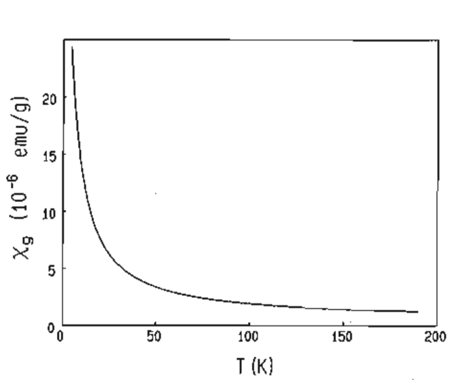

Figure 2. Magnetic susceptibility between 4.2 and 200 K showing clear Curie–Weiss behavior.

incorrect because χ_0 was assumed to originate only from core diamagnetism and the data were obtained only to 77 K.

The results of the susceptibility and EPR measurements, especially the small value of the Curie constant C_g, cannot be simply understood on the basis of the structure of Sc_7Cl_{10}. From C_g and the formula weight (fw) an effective magnetic moment per formula unit can be obtained: $\mu_{eff} = (8C_g(\mathrm{fw}))^{1/2} = 0.90\ \mu_B$. In systems with localized magnetic moments, $\mu_{eff} = g[S(S+1)]^{1/2}$. Since the EPR signal intensity increases approximately as $1/T$, we presume that this resonance arises from the magnetic moments that produce the Curie–Weiss susceptibility behavior and therefore that $g \approx 2$. In that case with $S = {}^1/_2$, μ_{eff} should be approximately 1.73 μ_B if there were one local moment per formula unit.

The lack of a resolved hyperfine structure of ^{45}Sc, which otherwise produces eight lines with a total splitting of ~400 G[1] in the EPR suggests that the line is narrowed by rapid spin diffusion, (i.e, these electrons have some mobility). This complicates possible interpretations of the source of the local moments. We note, however, that g values close to 2 have been observed for Sc^{2+} centers in a tetragonal crystal field with an occupied d_{z^2} orbital.[9]

There are three possibilities concerning the source of the observed spins: (1) the crystal structure is slightly distorted from that published[1] to produce one unique magnetic Sc site in *two* formula units; (2) interstitial impurities in the double-octahedral Sc chain, such as C, O, or H, add or subtract one-half of a localized electron per formula unit; (3) the moments are partially itinerant, and the moment is thereby reduced from that expected for localized moments. We consider each possibility briefly in turn.

First we consider a distorted crystal structure. This distortion would be small since none was detected in the structural determination.[1] If we use the measured g value and $S = {}^1/_2$, we obtain one magnetic state per 1.92 formula units. Here we assume that this is ideally 2.0 formula units within the limits of sample purity (e.g. small amounts of second phase) and the accuracy of the susceptibility measurements. That is, 1 in 14 Sc atoms would carry a magnetic moment, and this Sc would occupy a unique position in the unit cell. Note that the published unit cell contains two formula units, but the symmetry does not allow a single unique Sc site.

The second possibility is that interstitial species are present as impurities so that the true compound formulation would be $I_xSc_7Cl_{10}$, with $x = 0.5$ for I = H, ${}^1/_8$ for I = C, or ${}^1/_{12}$ for I = O (or odd multiples of these x). Such interstitials are known to exist in metal-rich compounds of the early transition metals but only at much higher levels, e.g. in $Sc_7Cl_{10}C_2$ in an ordered, related structure.[7] The detection of such a low level of impurities by X-ray diffraction or chemical analysis would be quite difficult, so their presence can not be ruled out. These impurities could either create localized moments on a nearby Sc or destroy such moments by tying them up in a covalent bond.

Lastly, it seems possible, especially in light of the narrowed Sc EPR line, that the magnetic moments are themselves itinerant; e.g., they take part in the metallic conduction. This could produce a moment below what is expected for a single localized electron for a formula unit.[11]

Summary

Sc_7Cl_{10} is found to be a good conductor and to contain local magnetic moments. The exchange between these moments is weak ($\Theta = 1.4$ K), but they must be somewhat mobile since the hyperfine structure of the EPR line is narrowed out. The EPR and magnetic susceptibility data cannot be simply understood on the basis of the structure and assumed purity of Sc_7Cl_{10}. Further chemical and physical studies are warranted.

Registry No. Sc_7Cl_{10}, 61966-52-7.

Supplementary Material Available: A listing of magnetic susceptibility data vs. temperature (1 page). Ordering information is given on any current masthead page.

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