

The Solution of Alkaline Earth Metals in Their Molten Halides. V. The Magnetic Susceptibility of Melts in the System Strontium-Strontium Chloride

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The magnetic susceptibility of melts at temperatures around 900°C in the system strontium-strontium chloride has been measured for concentrations up to 6.4 mol % strontium. A decrease in the diamagnetic susceptibility with increasing strontium metal content is observed. This paramagnetic effect is smaller than expected if Sr⁺-ions were formed. An alternative model is suggested, which presumes localized states not associated with well-defined chemical species.

The magnetic susceptibilities of melts in the systems barium-barium chloride and barium-barium bromide have previously been measured.¹ The results revealed that the addition of barium metal to molten barium chloride (or bromide) created a paramagnetic component in the melt. A paramagnetic component could conceivably arise by the formation of Ba⁺-ions in the mixture, since the Ba⁺-ions have an odd number of electrons. Not all experimental facts fit this hypothesis very well, and it was suggested that one should consider other models for the distribution of the two valence electrons from the barium metal. The need for more experimental data was emphasized, and we have therefore extended the susceptibility measurements to the strontium-strontium chloride system. Phase data by Staffanson² indicate appreciable solubility of strontium metal in the strontium chloride melt. The system exhibits a monotectic at 839°C with 5.5 mol % strontium metal.²

EXPERIMENTAL

Materials. Anhydrous strontium chloride EL grade was obtained from Merck. The manufacturer stated the following figures in per cent about contaminations: SrCl₂ ≥ 98.5, N < 1 × 10⁻³, Fe < 5 × 10⁻⁴, Ba < 1 × 10⁻², Ca < 1 × 10⁻¹. Prior to use, the salt was vacuum

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desiccated at 400°C for 10–12 h after which it was melted at about 900°C in an argon atmosphere. The strontium metal was provided as rods by Electronic Space Products, Inc. The manufacturer gives the following “typical analysis” for the strontium metal delivered: Sr 99 %, Ca 0.3 %, N₂ 0.05 %, Na, K, Li < 0.01 %, Ba 0.3 %, Mg 0.35 %, Al 0.02 %, Fe 0.05 %. The melting point is 770°C. The metal was cut in pieces and stored under dry toluene. Spectroscopically pure argon gas from Norsk Hydro was used as a protective atmosphere during all operations under preparation and measurement.

Procedure. The experimental technique and apparatus were the same as described previously.¹ The magnetic measurements were commenced at about 850°C, and readings were taken in intervals of a few degrees up to about 920°C. After the conclusion of each run, the sample was analyzed for its metal content by volumetric determination of the hydrogen gas evolved on dissolving the sample in 0.1 M hydrochloric acid. The result of the analysis agreed well with the “weighed in” amounts.

Our measurements of the density of melts in the system strontium-strontium chloride have been presented previously.³

RESULTS AND DISCUSSION

The experimental results, in the form of weight changes on removing the magnetic field, were converted to magnetic susceptibilities, using appropriate correction terms,² calibration values,² and previously measured densities.³ Thus obtained experimental susceptibilities at 900°C are given in Table 1.

Table 1. Molar magnetic susceptibilities, χ , (standard deviation 2.0 χ cgs/mol) of mixtures in the system Sr-SrCl₂ at 900°C.

N (mol % Sr)	$\chi \times 10^6$ (cgs/mol)
0	-64.1
2.21	-56.3
2.38	-54.0
3.45	-52.9
3.96	-52.1
5.98	-47.0
6.42	-46.8

Table 2. Theoretical molar susceptibilities, $\chi \times 10^6$, for various species.

Assumed species	$\chi \times 10^6$ (cgs/mol)
Sr ⁰	-83.9
Sr ⁺	-43.6 + 375 000/T
Sr ₂ ²⁺	-87.2
Sr ²⁺	-15.2
Cl ⁻	-25.8

The table gives the molar susceptibilities (one “mol” of mixture is here understood as the mixture, where the sum of the molar amounts of strontium chloride and strontium metal adds up to one). The susceptibilities did appear to have some temperature dependence within the limited temperature range used here (~70°C). However, within the limits of error of the equipment used, no reliable value for the temperature dependence was obtained.

Fig. 1 shows experimental values for the relative magnetic susceptibilities as a function of composition. The relative magnetic susceptibilities are defined as $\chi_{\text{rel}} = \chi_{\text{mixture}} - \chi_{\text{SrCl}_2}$. Fig. 1 shows that the relative value becomes more negative with increasing metal content. This system therefore behaves like the barium-barium chloride and the barium-barium bromide system.¹

Fig. 1 also shows the expected behaviour of the relative susceptibility for a number of different theoretical models. Theoretical molar susceptibilities for

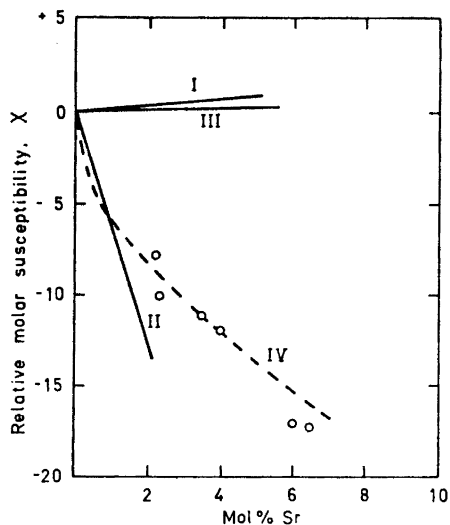


Fig. 1. Observed molar magnetic susceptibilities, χ , at 900°C compared with calculated curves from four different models. Circles: observed values. I: $\text{Sr} \rightarrow \text{Sr}^0$. II: $\text{Sr} + \text{Sr}^{2+} \rightarrow 2\text{Sr}^+$. III: $\text{Sr} + \text{Sr}^{2+} \rightarrow \text{Sr}_2^{2+}$. IV: Free electron in degenerate energy levels.

various species have been calculated from the Langevin equation⁴ (with Slater screening constants⁵) and the van Vleck equation.⁴ The theoretical susceptibility of the various species thus calculated are reported in Table 2. Assuming additivity of the susceptibilities for all species in a given model, theoretical curves may be obtained, allowing a comparison with the experimental values. The comparison in Fig. 1 shows that models involving only diamagnetic species in the solution (such as Sr_2^{2+} or Sr^0) do not fit the experiments. A model involving the formation of Sr^+ ions, on the other hand, gives a too large paramagnetic contribution. A model assuming the metal valence electrons to be "free", occupying degenerate states and obeying Fermi-Dirac statistics,^{1,6} gives a fairly good fit. This model gave a fair agreement also with the previously investigated systems.¹ The agreement is probably rather fortuitous, however, in view of the oversimplifications involved.

A brief summary of available evidence on the nature of the systems Me-MeX_2 , where Me is an alkaline earth metal and X is a halide, may be of interest at this point:

(α) Vapour pressure measurements⁷ and EMF measurements⁸ indicate that two foreign particles are formed for each Me atom dissolved in the melt.

(β) Density changes on dissolving the metal are not in accordance with the formation of Me^+ ions.³

(γ) The electric conductivity increases rapidly with metal addition,^{9,10} presumably due to the introduction of mobile electrons.

(δ) The previous¹ and present magnetic susceptibility measurements indicate the presence of unpaired electrons in the mixture.

Which model, then, is compatible with the above evidence? Obviously the evidence under (α) requires the two valence electrons from the metal to be localized in some way at separate sites. The implied dissociation of the pair of valence electrons is in agreement with evidence from magnetic measure-

ments (δ). The localization of the valence electrons is less sharp than the limiting case where the electron is localized on a Me^{2+} ion forming a Me^+ -ion. The absence of appreciable fractions of Me^+ ions is indicated by density data under (β). The electronic conductance indicate that the valence electrons are not very tightly bound in their traps, however.

The presently available evidence, reviewed above, suggests that some recent theoretical work¹¹ on energy levels of electrons in liquid metals could be pertinent to an understanding of these systems. The theoretical studies show that delocalized electronic conductance bands in ideal crystals tend to become localized by the introduction of disorder in the structure (*e.g.* by the melting process). This phenomenon seems to be of a general nature for excited states and has been extensively studied for vibration spectra.¹² It is plausible that the valence electrons of the dissolved alkaline earth metal could be trapped in states, localized as a result of the disorder in the liquid structure. These localized states are "physical" in the sense that they do not correspond to well defined chemical species. The model, of course, does not preclude the presence of smaller amounts of the chemical species type of electron traps in the melt, which may enter in various equilibria with the "localized electron" traps.

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REFERENCES

1. Grjothheim, K., Ikeuchi, H. A. and Krogh-Moe, J. *Acta Chem. Scand.* **24** (1970) 985.
2. Staffanson, L. I. *The Physical Chemistry of Metals in their Molten Halides, Ph.D. Thesis*, London University 1959.
3. Grjothheim, K., Ikeuchi, H. A., Dhabanandana, S. and Krogh-Moe, J. *Acta Chem. Scand.* **25** (1971) 3415.
4. Selwood, P. W. *Magnetochemistry*, Interscience, New York 1956.
5. Slater, J. C. *Phys. Rev.* **36** (1930) 57.
6. Dekker, A. J. *Solid State Physics*, Macmillan, London 1962.
7. Van Westenburg, J. A. *Ph.D. Thesis*, Iowa State University, Ames, Iowa 1964.
8. Grjothheim, K., Ikeuchi, H., Krogh-Moe, J. and Moser, Z. *Trans. Roy. Inst. Technol., Stockholm* 1972, No. 295, p. 601.
9. Emons, H. H. and Richter, D. *Z. anorg. allgem. Chem.* **353** (1967) 148.
10. Dworkin, A. S., Bronstein, H. R. and Bredig, M. A. *J. Phys. Chem.* **70** (1966) 2384.
11. Borland, R. E. In Temperley, H. N. V., Rowlinson, J. S. and Rushbrooke, G. S., Eds., *Physics of Simple Liquids*, North Holland Publishing Co., Amsterdam 1968, Chapter 16, p. 693.
12. Dean, P. and Bacon, M. D. *Proc. Phys. Soc.* **81** (1963) 642.

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