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The structure of molten $FeCl_3$ at 320°C has been measured with neutron diffraction at the Intense Pulsed Neutron Source. The results indicate that melting in $FeCl_3$ is accompanied by a change in local structure from the octahedral environment of the Fe^{3+} in the solid to an Fe_2Cl_6 molecular liquid. This behavior is similar to that observed in $AlCl_3$ and in contrast to that of YCl_3 where an octahedral coordination is preserved on melting.

INTRODUCTION

The halides of trivalent transition metals crystallize into a variety of structures, generally characterized by a rather close packing of the halide ions with the metal ions occupying the appropriate fraction of tetrahedral sites (1). On melting, they can assume radically different types of structure, either mimicking the close packed arrangement of the crystal or transforming into a more open, molecular type of structure. The different behaviors in melting can be inferred from the

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considerable range in changes in entropy ΔS and specific volume $\Delta V/V$, tabulated in Table I. For example, $FeCl_3$, with ΔS = 17.8 e.u. and $\Delta V/V$ = 0.63, contrasts dramatically with YCl_3 with ΔS = 7.6 e.u. and $\Delta V/V$ = 0.005. Our recent work on the structure of molten YCl_3 has shown that it does indeed melt into a close-packed structure, similar to the crystal but with some disordering of the Cl^- ions.(2). On the other hand, our studies of graphite intercalated with $FeCl_3$ have shown that the intercalated layers form a two-dimensional liquid of Fe_2Cl_6 molecules at higher temperatures, while at lower temperatures they form a close-packed hexagonal close packed arrangement similar to the bulk crystal. (3). The object of the present study was to make a careful measurement of the structure of the bulk liquid and determine whether the molecular structure is found here also, as suggested by the thermodynamic data of Table I.

NEUTRON DIFFRACTION EXPERIMENT

$FeCl_3$ material, 99.999% purity, obtained from APL Engineering Materials, Inc., was encapsulated in vitreous silica tubes 4mm I.D., 5mm O.D., 10 mm high with a loading sufficient to fill the beam height of 50mm when molten. Neutron diffraction measurements were carried out at the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source. The sample was heated to 320°C in a vacuum furnace inside a cylindrical vanadium element. The structure factor S(Q) was obtained after correcting the measured diffraction patterns for multiple scattering, absorption and inelastic effects using standard procedures (4). For the present sample, it was necessary also to subtract the paramagnetic scattering from the Fe^{3+}. This was calculated on the basis of the value of the magnetic moment of the free Fe^{3+} ion, 5.92 μ_B (5) and the published free-ion form factor (6).

The corrected structure factor S(Q) is shown in Fig. 1. Strictly speaking this represents a weighted average of the three partial structure factors:

$$S(Q) = 1/\langle b\rangle^2 \Sigma_{ij} (c_i c_j)^{1/2} b_i b_j S_{ij}(Q) - \langle b^2\rangle/\langle b\rangle^2 + 1 \qquad (1)$$

However, the scattering lengths of Fe and Cl are nearly identical, so S(Q) is very close to the Bhatia-Thornton number density structure factor

$$S_{NN}(Q) = \Sigma_{ij} (c_i c_j)^{1/2} S_{ij}(Q) \qquad (2)$$

It exhibits a three-peak structure with peaks at wave vectors Q = 0.95, 2.05, and 3.67 $Å^{-1}$, respectively. Scaling with the nearest-neighbor distance $r_1 \approx 2.28$ Å (see below), these values correspond to scaled wave vectors $Qr_1 \approx 2.2$, 4.7, and 8.4, respectively, typical of values found for the first sharp diffraction peak, the Coulomb peak and the hard sphere peak, respectively, in complex liquids (7).

The total pair correlation function in real space T(r), obtained by Fourier transformation of S(Q), is shown in Fig. 2. It has a well-defined first peak which can be fitted by two gaussian functions centered at 2.19 and 2.37 Å. These values are about 4% larger than the Fe-Cl separation observed for terminal and bridging Cl- ions in Fe_2Cl_6 molecules in the vapor.(8). Converting T(r) to the radial distribution function n(r) gives a total area for the first peak of 1.8; this corresponds to an average coordination number of 3.6 about the Fe^{3+} ions, slightly lower than the value of 4.0 for the isolated molecule. The octahedral coordination found in the crystalline phase is clearly ruled out. There is some possibility of dissociation in molten $FeCl_3$, leading to $FeCl_2$ and free Cl_2 (9); however, in the present experiment, since S(Q) is normalized to 1.0 at high Q, values of the coordination number about the Fe^{3+} ions would be 33% higher than those observed, so this is also inconsistent with the data. Thus, these data show unambiguously that the bulk melt is a molecular liquid composed of Fe_2Cl_6 molecules.

The second peak in T(r) is a broad peak with an area in n(r) of 5.9, presumably due to Fe-Fe and Cl-Cl correlations. The isolated Fe_2Cl_6 molecule would give a value of 3.0, so that approximately half the second-neighbor correlations are inter-, as opposed to intra-, molecular. The measured value is, again, considerably lower that the value which applies for the closed-packed structure of the crystal, 9.25.

CONCLUSIONS

The results of these measurements indicate that melting in $FeCl_3$, associated with a large (63%) volume change, is accompanied by a change in local structure from the octahedral environment of the Fe^{3+} in the solid to an Fe_2Cl_6 molecular liquid.

A suggested geometry of the structural transition is shown in Fig.3. Each Fe^{3+} ion undergoes a substantial displacement, from an octahedral site between two triangles of Cl^- ions in adjacent planes, shown in the lower part of the figure, to a tetrahedral site between one Cl^- triangle and the Cl^- opposite it in the adjacent plane, as observed in the molecular crystals $AlBr_3$ (10) or $GaCl_3$(11), shown in the upper part of the figure. At the same time there must be a decrease in the packing of the Cl^- to account for the volume expansion. The reduced value for the second-neighbor coordination number observed in molten $FeCl_3$ is consistent with this reduction in Cl^- packing. Melting in $FeCl_3$ is clearly similar to that observed in $AlCl_3$ and in contrast to that of YCl_3 where an octahedral coordination is preserved on melting.(2).

Results of detailed model calculations on the structure of molten $FeCl_3$ are in progress and will be reported in a forthcoming publication (12).

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TABLE I.

Physical properties of some trivalent metal chlorides[a]

Salt	T_m(K)	ΔS_m(e.u.)	$\Delta V/V^b$	$\sigma(\Omega^{-1}cm^{-1})$
$InCl_3$	859	----	0.61	0.42
$AlCl_3$	466	18.1	0.88	$5x10^{-7}$
$GaCl_3$	351	7.4	0.17	$2x10^{-6}$
$BiCl_3$	505	5.0	0.22	0.38
$SbCl_3$	347	8.7	0.17	$2x10^{-4}$
YCl_3	994	7.6	0.005	0.39
$FeCl_3$	577	17.8	0.63	---

[a]After M.P.Tosi, G. Pastore, M.-L. Saboungi, and D. L. Price, *Physica Scripta*, **139**, 367 (1991)

[b]Relative difference of specific volume of liquid at T_m and that of solid at room temperature

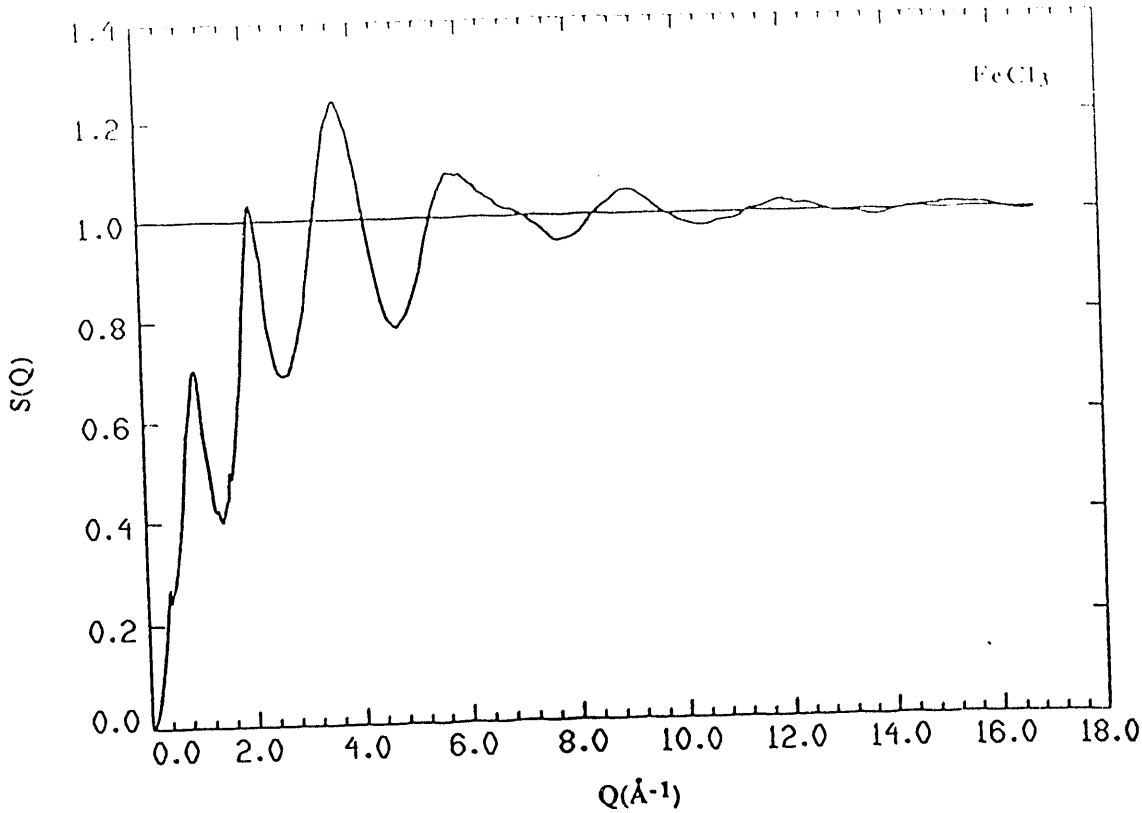

Fig. 1. Measured stucture factor of molten $FeCl_3$ at 320°C

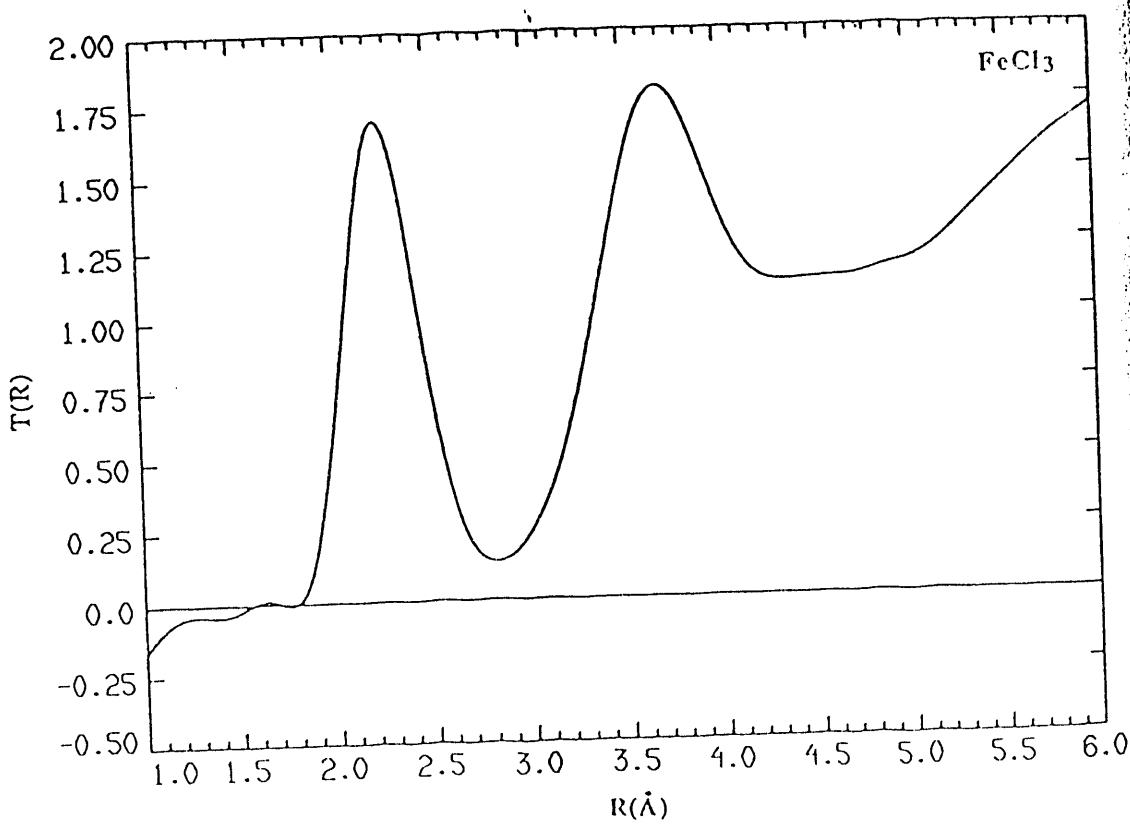

Fig. 2. Pair correlation function of molten $FeCl_3$ at 320°C.

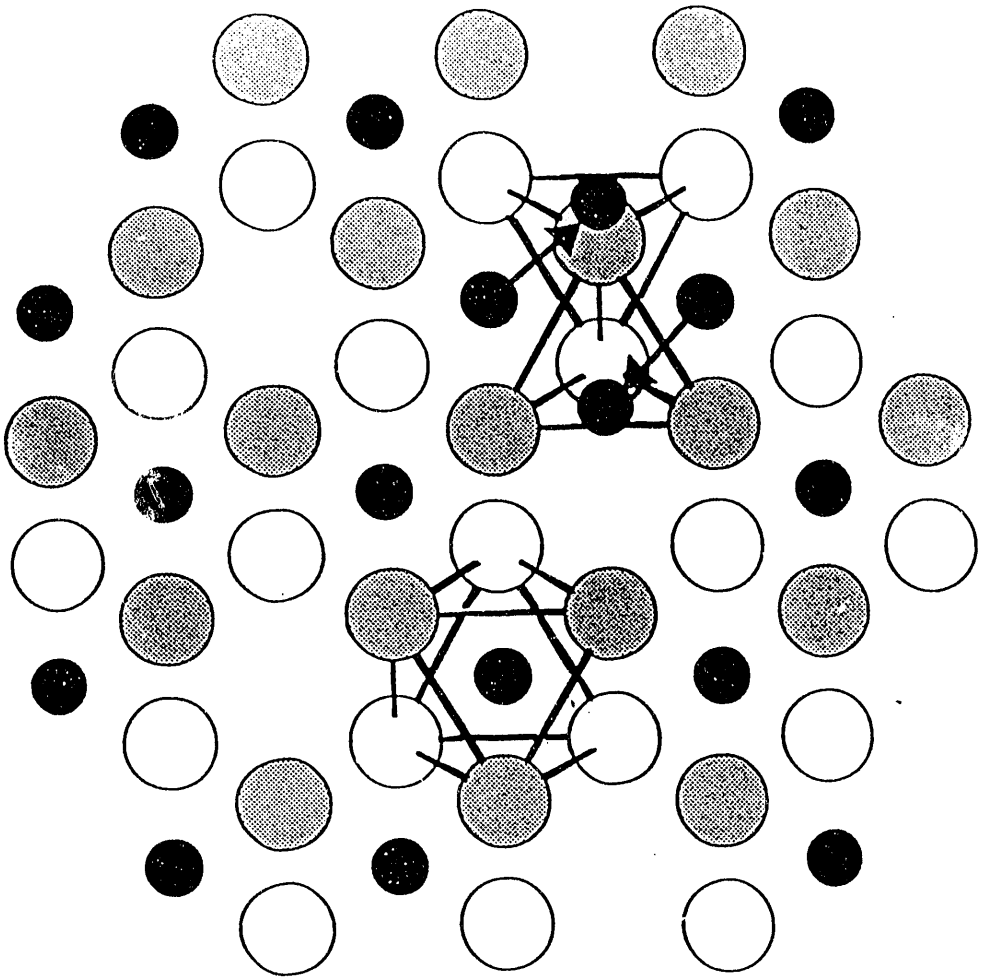

Fig. 3. Schematic illustration of melting in $FeCl_3$. The black spheres represent a plane of Fe^{3+} ionsin the crystal, and the grey and white spheres represent planes of Cl^- ions above and below the plane of Fe^{3+} ions, respectively. The lower cluster represents the octahedral coordination of the Fe^{3+} ions in the crystal, and the upper cluster the Fe_2Cl_6 molecule in the melt. The arrows indicate the required displacement of the two Fe^{3+} ions upon melting.

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