Magnon Sideband Profiles and Structural Distortions in Organic-intercalated Mn^{II} Layer Perovskite Halide Salts

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The absorption band profiles of the magnon sideband associated with the lowest energy component of $^6A_{1g} \rightarrow {}^4T_{1g}(D)$ have been measured in the two-dimensional antiferromagnets $(RNH_3)_2MnCl_4$ (R = Me, Et, Pr^n, $PhCH_2$) to correlate the bandshape with the extent of puckering in the Mn–Cl layers; no simple correlation exists with any single crystallographic parameter.

Layer perovskite halide salts with general formulae $(RNH_3)_2MX_4$ (R = alkyl or aryl; M = Cr, Mn, Fe, Cu, Cd; X = Cl, Br) have been widely studied from two points of view. First, they provide simple model systems of two-dimensional ferro- or antiferro-magnetism since their structures are built up from layers of corner-sharing octahedra separated by the extended chains of the RNH_3^+ cations.[1,2] Second, they undergo structural phase transitions driven by variations in the arrangement of the hydrogen bonds that link the $-NH_3$ groups to the apical and equatorial Cl ions.[3] They are also examples of what we have called 'molecular composites',[4] namely crystals containing alternating organic and inorganic groups whose properties combine those of organic molecular and inorganic ionic solids. In this communication we demonstrate that in the Mn layer perovskite halide salts exciton–magnon absorption band profiles are extremely sensitive to variation of the intercalated organic groups which cause minor distortions of the Mn–Cl layers.

Because of the requirements of the hydrogen bonding, and the packing of the organic sidechains, the M–Cl layers in these salts are not planar, except in the 'high temperature tetragonal' phase when the NH_3 groups rotate freely and the organic chains 'melt'. At lower temperatures the layers become puckered so that adjacent MCl_6 octahedra are tilted alternately to either side of the normal to the plane through the metal atoms. One result is that what would otherwise be simple collinear antiferromagnets show a degree of spin canting, which would be expected to correlate with the puckering observed crystallographically. In the methyl-, ethyl- and n-propyl-ammonium tetrachloromanganate salts in particular, sharp peaks observed at the Neel temperature in the initial susceptibility[5,6] have been attributed to weak ferromagnetism arising from spin canting. In the n-propylammonium salt, where the spins lie perpendicular to the basal plane, it was estimated that they are canted about 0.05° away from the

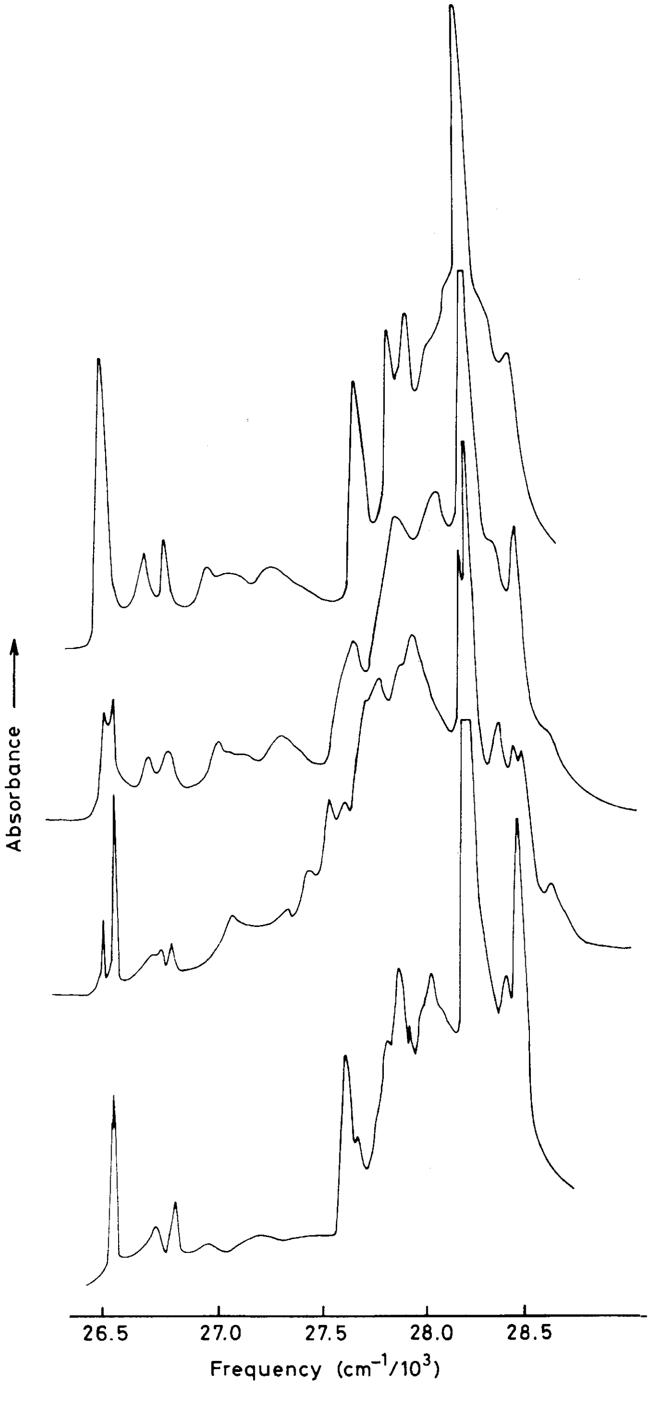

Figure 1. $^6A_{1g} \rightarrow {}^4T_{1g}(D)$ region in $(RNH_3)_2MnCl_4$ at 4.2 K. Top to bottom: R = Me, Et, Prⁿ, $PhCH_2$.

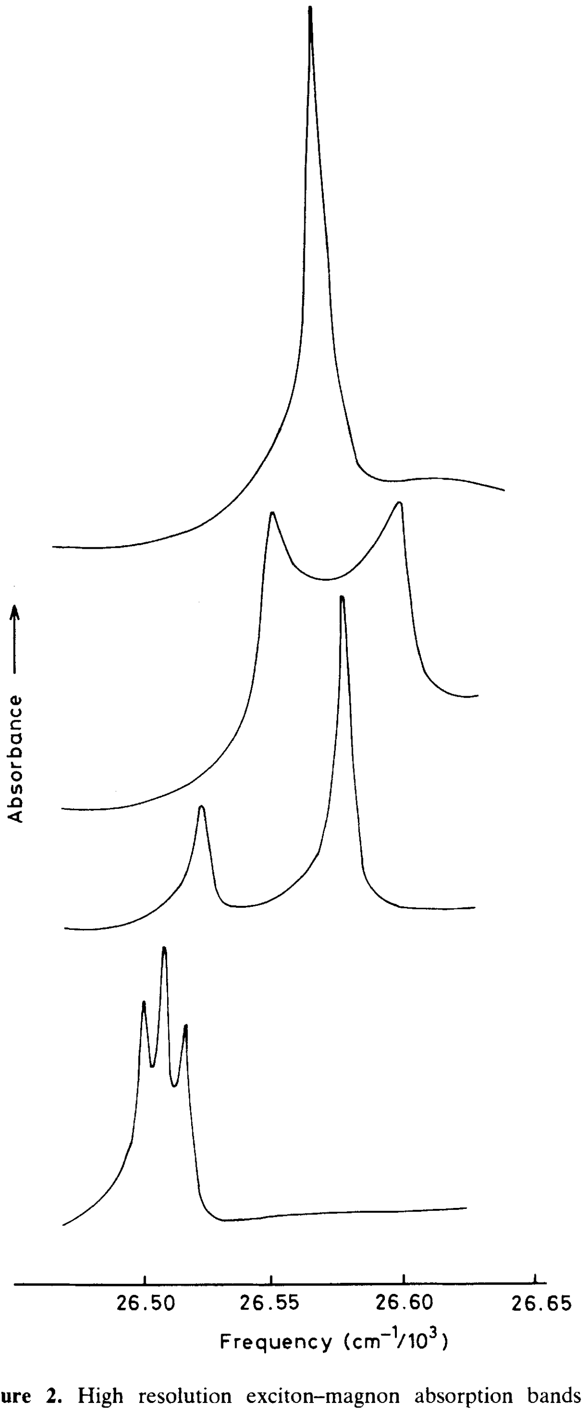

Figure 2. High resolution exciton–magnon absorption bands in $(RNH_3)_2MnCl_4$ at 4.2 K. Top to bottom: R = Me, Et, Prⁿ, $PhCH_2$.

Table 1. Bond angles in A_2MnCl_4 (defined in the text) and exciton–magnon band frequencies.

A	Temperature[a]/°C	θ/°	ϕ/°	ψ/°	Frequency (cm^{-1})
Rb	295 (*X*)[b]	0	0	0	26552
$MeNH_3$	188 (*X*)[c]	7.48(av.)	7.49	10.5	26578
$EtNH_3$	126 (*X*)[d]	14.0	8.76	17.51	26557, 26579
Pr^nNH_3	180 (N)[e]	12.2	8.35	16.7	26528, 26580
$PhCH_2NH_3$	—	—	—	—	26502, 26509, 26518

[a] *X* = *X*-Ray; N = neutron. [b] Ref. 9. [c] Ref. 12. [d] Ref. 13. [e] Ref. 14.

normal to this plane giving a small ferromagnetic component parallel to the plane.[6]

In a collinear antiferromagnet, exciton transfer only takes place on one sublattice, because intersublattice transfer is forbidden by non-conservation of the spin angular momentum. However, spin canting removes this constraint and both intra- and inter-sublattice transfer can occur. Kojima *et al.*[7] attributed the anomalous double-humped structure of a magnon sideband arising from one of the components of the $^6A_{1g} \rightarrow {}^4T_{1g}(D)$ transition in $(EtNH_3)_2MnCl_4$ to a splitting of the exciton (Davydov splitting) by inter- and intra-sublattice transfer. Since the magnitude of the matrix element for intersublattice transfer is proportional to the square of the spin canting angle,[8] the shape of the magnon sideband should be a sensitive probe of the way in which the structure of the metal halide layer accommodates to variations in the organic substituents. We have therefore recorded spectra of several $(RNH_3)_2MnCl_4$ salts in the region in question. We conclude that the band profiles are indeed extremely sensitive to small changes in the bond angles but that there is no simple correlation with any single crystallographic parameter.

Absorption spectra were measured at 4.2 K using a McPherson RS10 spectrophotometer with an Oxford Instruments CF100 continuous flow cryostat. The spectral bandpass was 0.1 Å (about 0.6 cm^{-1} at the wavelength in question). Unpolarised light was incident normal to the Mn–Cl layers, corresponding to the axial orientation in the high temperature tetragonal phase. Polarised spectra at lower resolution show that the transition in question is electric dipole allowed with the electric vector parallel to the basal plane. Figure 1 shows the whole of the $^6A_{1g} \rightarrow {}^4T_{1g}(D)$ region and Figure 2 the zero-phonon region near 26 500 cm^{-1}, in the R = Me, Et, Pr^n, and $PhCH_2$ salts. In each example we observe highly asymmetric band profiles characteristic of exciton–magnon combinations, but with very different fine structure. It is also worth noting that in Rb_2MnCl_4, with the K_2NiF_4 structure,[9] which can be considered as a prototype of the high temperature tetragonal phase of the layer perovskite salts, the corresponding electronic origin[10] consists of a single peak at 26 352 cm^{-1} with a halfwidth and asymmetry very similar to that shown in Figure 2 for $(MeNH_3)_2MnCl_4$.

Extensive crystallographic data are available for the three alkylammonium salts at various temperatures but no positional parameters exist for the benzylammonium salt. There are several possible indices of the puckering of the Mn–Cl layers.[11] These include the deviation of the Mn–Cl–Mn angle with the basal plane from 180° (θ), the tilt of the axial Mn–Cl bond from the normal to the mean plane (ϕ), and the deviation of the Cl–Cl–Cl angle joining neighbouring equatorial $MnCl_4$ squares from 180° (ψ). Table 1 collects all three of these with the frequencies of the exciton–magnon bands near 26 500 cm^{-1}. We note that the layers in $(MeNH_3)_2MnCl_4$ are puckered according to all three criteria, though there is only a single exciton–magnon peak near 26 500 cm^{-1}, suggesting negligible intersublattice exciton transfer. However, the mean θ is much smaller than in the other two compounds because the γ-phase, whose structure was determined at 188 K, has alternate θ angles of 0 and 14.96°. There is appreciable puckering of the layers in all three alkylammonium salts, slightly greater in the $EtNH_3$ salt than in the other two, by all three indices. Increasing magnitude of intersublattice transfer will increase the separation between the two exciton branches, but experimentally the separation between the two exciton–magnon peaks is largest in the Pr^nNH_3 salt. In the $PhCH_2NH_3$ salt the three peaks could arise from singularities in the combined exciton–magnon densities-of-states at the X and M point of the two-dimensional Brillouin zone,[7] but further comment must await information on the crystal structure. In general, it is surprising that variations in remote organic substituents should have such a striking effect on ligand field absorption spectra, and we are examining further members of this set of salts, including more bulky substituents, to chart the small structural changes which bring about the effect.

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