

the f_a^j , f_b^j (perhaps by parameterization) this additional information would appear in the above derivation as an added constraint.

After completion of the present work there appeared a paper by Pollak and Levine⁴ with an approach to the problem very similar to that of the present note. However, instead of maximizing the probability they maximize the entropy of the system and, among other results, obtain Miller's UST exactly for both symmetric and asymmetric cases.

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¹(a) W. H. Miller, *J. Chem. Phys.* **65**, 2216 (1976); for a derivation with notation more akin to the present see (b) E. Pollak and P. Pechukas, *J. Chem. Phys.* **70**, 325 (1979).

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The crystal structure of the noble gases^{a)}

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It is an old problem to understand why matter tends to be in a crystalline state at low temperature. There has been some recent progress but only for molecular bonding and only for one and two dimensional models.¹⁻⁶

However even assuming that a specific material should be crystalline there can still be difficulty in predicting the correct crystal structure. Consider the heavier noble gases, excluding the unique case of helium. Using the usual Lennard-Jones interaction one expects the ground state (i. e., zero temperature, zero pressure) to be close packed with most (~75%) of the energy per particle coming from the twelve nearest neighbors and six next-nearest neighbors. Restricting attention to the best known close packed structures, the face-centered-cubic (fcc) and hexagonal-close-packed (hcp), which of course differ only in the distribution of third and higher nearest neighbors, it would seem that long range effects would have to be considered in order to differentiate between the structures. When the Lennard-Jones potential is used to take into account the long distance contribution one finds that the hcp structure has a slightly lower (0.01%) energy per particle, leading one to expect a thermodynamic preference for the noble gases to crystallize in the hcp structure.⁷ Since they do not, but strongly favor the fcc structure,⁸ a number of possible "explanations" have been put forward, none of which, however, have found broad support in the literature.^{9,10}

We wish to point out one aspect of the problem which is conceptually elementary but which seems to have been overlooked, namely the different *surface* energies of

finite samples of the two structures, due to the different geometry of surfaces available as faces.

In the most naive model, taking into account only nearest neighbor bonds, Wulff's construction^{11,12} yields the lowest energy shapes for finite samples of the two crystal structures.¹³ Then a straightforward computation of the number of bonds for N atoms in each structure gives:

$$B_{fcc} = 6N - 2^{1/3} 6N^{2/3} + O(N^{1/3}),$$

$$B_{hcp} = 6N - 3(65/4)^{1/3} N^{2/3} + O(N^{1/3}).$$

Thus there is a 0.5% lower surface energy per particle for the fcc structure (and identical volume energy in this nearest neighbor model; it might be preferable to consider *all* neighbors for the surface effect, but this seems to be difficult). For a small crystal, up to about 175 000 atoms or 230 Å diameter, this "short range" surface effect dominates the "long range" volume effect and provides the needed explanation: assuming the crystal grows from a (solid but noncrystalline¹⁴) nucleus, and settles into a crystal structure when in the range of 100-1000 atoms,¹⁵ it is now understandable that the material should crystallize in fcc and not be able to fluctuate to the hcp structure even after further growth beyond the 10⁸ atom size.

Finally we note that our result holds away from zero temperature and pressure by arguments detailed in Barron and Domb.¹⁶

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Another look at the EPR of Cr^{3+} in $(\text{NH}_4)_x \text{Ti}_{1-x} \text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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In a recent study of the EPR of Cr^{3+} in the alum series, $(\text{NH}_4)_x \text{Ti}_{1-x} \text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, V. K. Jain presented evidence indicating that the variation of the zero-field splitting parameter D with composition is almost linear.¹ This would imply that the trigonal distortion about the chromium ion (at the Al site) depends on the average occupancy of neighboring M^{1+} sites or that the distortion follows the lattice spacing which has been shown to vary linearly with composition in this system.² Neither of these suppositions is in accord with previous studies of chromium(III) complexes which indicated that local distortions of the primary coordination shell of the paramagnetic ion control the zero-field splitting.³ The lattice spacing as determined by x-ray diffraction is an average over many spacings whereas the zero-field splitting reflects the local environment of $[\text{Cr}(\text{OH}_2)_6]^{3+}$. Thus one would expect a different EPR spectrum for each set of mixed near neighbors and perhaps further differentiation due to second neighbor substitutions. The six near neighbor M^{1+} sites about an M^{3+} are octahedrally disposed while the second neighbor M^{1+} sites are eightfold cubic. The expected variation of EPR spectra with composition is a sequential growth and diminution of discrete spectra corresponding to specific configurations of near neighbors. With this perspective we decided to re-examine the EPR of chromium(III) doped ammonium-thallium alum mixtures using powder techniques which allow rapid and accurate determinations of the zero-field splittings in a large number of samples.

Mixed crystal alums were prepared by evaporation of aqueous solutions of the component alums with added chromic sulfate. Each powdered EPR sample was obtained by grinding an individual untwinned crystal. After EPR spectra were taken, these samples were analyzed for thallium, aluminum, and chromium by atomic absorption or emission. Chromium concentrations varied from 0.7% to 2.5% of the aluminum. EPR spectra were obtained with a Varian E 12 system at 9.5 GHz and mag-

netic fields were measured with an NMR Gaussmeter.

The most important result of this study was the observation of multiple spectra for all samples with thallium concentration between 30% and 95%. Figure 1 contains a clear example of such multiple spectra with good resolution of two lines in the low field parallel feature of the powder pattern and obvious, if unresolved, splitting of the high field component. The low field parallel feature can be fitted with two Lorentzian lines of



FIG. 1. Powder EPR spectrum of $(\text{NH}_4)_x \text{Ti}_{1-x} \text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ $x=0.639$, 1.8% Cr, $\nu=9.502$ GHz, $T=299$ K, $g=1.974$, $D_1=582(2)$, $D_2=614(2)$. The parallel features are amplified $\times 40$. Separation of the low field peaks is 66 G and the entire trace spans 2900 G.