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LETTER TO THE EDITOR

On the theory of transitions in some molecular crystals II

In a previous letter [1]) (to be referred to as I) a suggestion was made about the character of the transitions which are found in the crystals of N_2 and CO at low temperatures and a possible way to calculate the temperatures and heats of transition was proposed. These transitions, taking place between a face centered cubic (f.c.c.) structure (α-form; stable at the lowest temperatures) and a structure of hexagonal close packing (h.c.p.) (β-form; stable above the transition temperature) were ascribed to differences in orientational order between the two crystal structures.

The main contributions to the orientational part of the interaction field of both the N_2 and CO molecules are due to quadrupole orientation effects and to anisotropy in the dispersion forces.

Calculations were proposed to be carried out on the basis of the central field approximation (c.f. ref. 2). This approximation is based on the following assumptions:

a) each molecule takes on its orientations in the average field of its neighbors.

b) the probability that the *i-th* molecule has its axis oriented within the solid angle $d\omega_i$ about the direction (θ_i, φ_i) is given by $f(\cos\theta_i)d\omega_i$; θ_i is measured with respect to a fixed direction characteristic for the *i-th* lattice site, being the direction of the molecular axis at absolute zero.

c) $f(\cos\theta_i)$ is the same for all the molecules.

The analysis leads to a consistency equation from which $f(\cos\theta_i)$ can be found as a function of temperature. From f all the thermodynamic quantities of the crystal can be derived. This calculation thus requires knowledge of what we will call the "zeropoint configuration" i.e. the orientations of the molecular axes at absolute zero.

In the central field approximation no clear distinction can be made between the f.c.c. and h.c.p. lattices because 1. each molecule in both lattices is surrounded by the same number of nearest neighbors and 2. the specific structure of the lattice is only used to a limited extent in the analysis. Therefore, the main distinction between crystal structures having f.c.c. or h.c.p. symmetry is, in this approximation, contained in the difference in zeropoint configuration exhibited by these structures. On the other hand, however, there may be various stable zeropoint configurations compatible with one and the same lattice structure. Although the configuration having the lowest energy, will constitute the stable phase in the vicinity of absolute zero, it is by no means impossible that at a higher temperature the crystal, while preserving the lattice symmetry, will make a transition to a phase corresponding to a different zeropoint configuration or to a disordered mixture of orientations of the molecular axes. Since measurements have in general been made at a few fixed temperatures only, the existence of such transitions cannot be excluded on experimental grounds. This state of affairs makes a complete treatment of the problem practically impossible since almost nothing is known about the possible zeropoint configurations. It thus follows, that the internal field method does not make a clear distinction between transitions which take place under preservation of either the f.c.c. or h.c.p. symmetry and transitions in which the lattice structure changes also, as is the case with the observed transitions in the crystals of N_2 and CO.

A calculation was made of the free energies of rotation as functions of temperature for the f.c.c. structures of both the N_2 and CO crystals, using the above mentioned interaction. In this calculation, the zeropoint configuration given by Vegard[3]), according to which the molecular axes are oriented parallel to the body diagonals of the cube (symmetry axes of the lattice), were used as a starting point. Although Vegard's experiments do not seem to be completely conclusive in determining the zeropoint configuration, there is further evidence which supports his result. Firstly, his configuration is stable at absolute zero and furthermore the quadrupole moments of N_2 and CO, which have been determined by Jansen, Michels and Lupton[4]) from crystal sublimation energies, using Vegard's configuration, agree very well with values found by entirely different methods[5]).

A similar calculation as was made for the f.c.c. structures, could not be carried out for the h.c.p. structures of N_2 and CO because of the lack of any information about the zeropoint configuration in these structures. For, measurements above the transition temperatures have shown that the molecules are either in a state of (practically) free rotation at these temperatures[6]), [7]) [8]), or oriented disorderly. Furthermore, although symmetry suggests a configuration in which the molecular axes are oriented along the symmetry axes of this lattice, this configuration is found to be instable at absolute zero.

The result of the calculation about the f.c.c. structures is the following. It was found that these structures of both crystals show a temperature above which the consistency equation, appearing in the analysis, does have no other solution than the trivial one. The latter corresponds to free rotation of the molecules. This would mean that if the f.c.c. structure with the same zeropoint configuration were also stable above this temperature, the crystal would exhibit a transition from hindered rotation to a freer form of rotation at this temperature; this is essentially an order-disorder transition. The appearance of such a transition is a consequence of the special type of molecular interaction only and is not affected by the crystal symmetry: other zeropoint configurations (also in a h.c.p.-structure) would give the same.

In the following table the calculated transition temperatures of these order-disorder transitions ($T_{tr(o-d)}$) in the f.c.c. lattice are compared with the observed transition temperatures of the α—β transitions ($T_{tr(\alpha-\beta)}$). The calculations were carried out with two different values for the molecular quadrupole moments Q: (*a*) those calculated by Jansen, Michels and Lupton[4]) and (*b*) values derived from microwave collision diameters[5]). γ is the anisotropy factor of the polarizability.

TABLE I

	γ[9])	$Q \times 10^{26}$e.s.u. (crystal)	$Q \times 10^{26}$ e.s.u. (microwave)	$T_{tr(\alpha-\beta)}$ °K exp.	$T_{tr(o-d)}$ °K theor.with(*a*)	$T_{tr(o-d)}$ °K theor.with(*b*)
N_2	0.187	1.27	1.49	35.61	29	47
CO	0.168	1.71	1.58	61.57	71	59

The calculated $T_{tr(o-d)}$ is seen to be critically dependent on the value of the quadrupole moment, showing a strong increase with increasing Q. A similar dependence on Q is exhibited by the observed transition temperature, when one compares the cases of N_2 and CO. As was pointed out in I, this behavior can be understood when one compares the contributions to the sublimation energy of the two types of interaction involved. The above mentioned result of the calculation, therefore, is in agreement with and corroborates the argument given in I. (The decrease of the transition temperature with increasing γ which could be understood on the basis of the same argument, also follows from these calculations. This is not brought out in the table because only one value of γ was used).

The agreement between the observed values of $T_{tr(\alpha-\beta)}$ and the the calculated values of $T_{tr(o-d)}$ is quite suggestive when taking into account all the limitations of the method of calculation (e.g. the fact that only one zero point configuration was used). Since, furthermore, Ruhemann[6]), Vegard[7]) and Taconis[8]), have found that the molecules are in a state of (practically) free rotation in the h.c.p. structures of N_2 and CO, one may conclude that the transitions take place from a state of relative orientational order in de f.c.c. structure to a state of orientational disorder in the h.c.p. structure, the latter having a lower free energy than the state of disorder in the f.c.c. structure.

A comparison of the states of free rotation in the f.c.c. and h.c.p. structures, however, cannot be carried out on the basis of the central field approximation. In this approximation, all differences between the e.c.c. and h.c.p. structures disappear as soon as free rotation sets in. Hence a complete treatment of the transitions under consideration cannot be given with the internal field method. On the other hand, no description of the transition mechanism for the lattice structure will be complete without a consideration of the situation below the transition temperature. Such a description, however, will be seriously hampered by the lack of information about the possible zeropoint configurations in the h.c.p. structure.

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