

Comments on group theoretical analysis of NQR spectra of crystals

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The use of generating function methods for the number of NQR lines of crystals exhibiting distortion is outlined. The intensity ratios of NQR lines can be obtained using a double coset method.

Key words: Group theory—NQR spectra of crystals.

1. Introduction

NQR spectroscopy of crystals uses a quadrupolar nucleus as a probe to detect and estimate electric field gradients in crystals [1–2]. The electric field gradient is very sensitive to the environment. A problem in interpreting complex NQR spectra of crystals is to theoretically obtain the NQR spectral pattern which should include the number of NQR lines and their intensity ratios in a given crystalline environment. NQR frequency is so sensitive to minute differences in electric field gradients that this method can be employed as a powerful tool in investigating crystals exhibiting phase transition. At the critical temperature T_c where the phase transition occurs the symmetry of the crystal usually changes. This in turn is reflected in the NQR spectra of such crystals. It will be very useful to have an easy theoretical method to obtain NQR spectral patterns so that given the symmetry of the unit cell of the crystal under consideration, one can predict the NQR spectral patterns. Conversely, the method should be of immense use in assigning the symmetries of the various phases with reference to phase transition.

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The objective of this paper is to develop a powerful group theoretical method which employs generating function methods to obtain the number of NQR lines of crystal for various unit cell symmetries. Further, a double coset method is used to obtain the intensity patterns. The present author [3, 4] has developed such generating function methods for the number of NMR lines. Using the generalized wreath product formalism developed by the author [5], the dynamic NMR spectra of non-rigid molecules can also be studied [6]. Balaban and Pomponiu [7] have developed similar combinatorial methods to obtain ESR spectral patterns. Randić and co-workers [8, 9] have developed topological methods for correlating chemical shifts. Thus it is not surprising that NQR spectral patterns of crystals exhibiting phase transition can be studied using topological and group theoretical methods. Sutton and Armstrong [12] have recently studied the halogen NQR spectra of crystals. They have used the Frobenius theorem to correlate the symmetry species spanned by nuclei from a bigger to smaller group to predict the NQR spectral patterns. We show here how this can be done without the knowledge of character spanned by nuclei. Further, they have not provided a rigorous method for the intensity patterns. We describe a double coset method for this problem.

2. Generating function methods

Let G be the point group corresponding to the space group of the crystal. Let D be the set of nuclei. Then each operation $g \in G$ can be considered as a permutation or permutation-inversion operation on D . Let R be a set containing just 2 elements denoted by α_1 and α_2 . Let f_i be a map from D to R defined as follows:

$$\begin{aligned} f_i(d_j) &= \alpha_1 & \text{if } i \neq j, d_j \in D \\ &= \alpha_2 & \text{if } i = j. \end{aligned}$$

Two maps f_i and f_j ($i \neq j$) are equivalent if there is a $g \in G$ such that

$$f_i(gd) = f_j(d) \quad \text{for every } d \in D.$$

The above relation can be seen to be an equivalence relation and hence the group G divides the set F of all maps from D to R into equivalence classes. It can be easily seen that the equivalence classes of F are the equivalence classes of nuclei. This is because if f_i and f_j are equivalent then the nuclei d_i and d_j are also equivalent. With each $r \in R$ let us associate a weight $w(r)$ which is just a formal symbol used to record the number of α_1 's and α_2 's in a given map. For example, with α_1 we can associate a weight α_1 and with α_2 we can associate a weight α_2 . Define the weight of any $f \in F$ as

$$W(f) = \sum_{d \in D} w(f(d)).$$

Thus the weight of any map f_i defined above is $\alpha_1^{N-1}\alpha_2$ if N is the number of nuclei in D . Pólya [10] proved a theorem now well-known as Pólya's theorem which gives a generating function for the equivalence classes of maps. Define the

cycle index of a group G as

$$P_G = \frac{1}{|G|} \sum_{g \in G} x_1^{b_1} x_2^{b_2} \cdots$$

if a $g \in G$ generates b_1 cycles of length 1, b_2 cycles of length 2 etc. on its action on the set D . To illustrate, the C_4 operation of the group O_h has the permutation representation (1)(6)(2345). Thus one can associate with this the term $x_1^2 x_4^1$ (2 cycles of length 1 and 1 cycle of length 4) in the cycle index. The cycle index polynomial of the group O_h acting on the 6 vertices of an octahedron can be seen to be

$$P_{O_h} = \frac{1}{48} [x_1^6 + 8x_3^2 + 9x_1^2 x_2^2 + 6x_1^2 x_4 + 7x_2^3 + 8x_6 + 3x_1^4 x_2 + 6x_2 x_4]$$

Pólya's theorem gives a generating function for the equivalence classes of maps by the following substitution in the cycle index.

$$\text{G.F.} = P_G \left[x_k \rightarrow \sum_{r \in R} w(r)^k \right].$$

The coefficient of $\alpha_1^{N-1} \alpha_2$ (N being the total number of nuclei) gives the number of equivalence classes of nuclei under the action of G for any group G .

Let us illustrate with the examples of fluorine NQR spectrum of antiferroite crystals with O_h symmetry. The cycle index for this case was already obtained. Since the weights of the elements in the set R are α_1 and α_2 we replace every x_k in the cycle index by $\alpha_1^k + \alpha_2^k$. This replacement yields the following generating function.

$$\begin{aligned} \text{G.F.}_{O_h} = \frac{1}{48} [& (\alpha_1 + \alpha_2)^6 + 8(\alpha_1^3 + \alpha_2^3)^2 + 9(\alpha_1 + \alpha_2)^2 (\alpha_1^2 + \alpha_2^2)^2 \\ & + 6(\alpha_1 + \alpha_2)^2 (\alpha_1^4 + \alpha_2^4) + 7(\alpha_1^2 + \alpha_2^2)^3 + 8(\alpha_1^6 + \alpha_2^6) \\ & + 3(\alpha_1 + \alpha_2)^4 (\alpha_1^2 + \alpha_2^2) + 6(\alpha_1^2 + \alpha_2^2) (\alpha_1^4 + \alpha_2^4)]. \end{aligned}$$

The coefficient of $\alpha_1^5 \alpha_2$ in the above expression is 1 indicating that all the nuclei are equivalent under the O_h symmetry. Let us consider the same crystal with distortions. Consider the same 6 nuclei in C_{4h} and C_i subgroups of the O_h group. The cycle indices for C_{4h} and C_i are shown below.

$$\begin{aligned} P_{C_{4h}} &= \frac{1}{8} [x_1^6 + 2x_1^2 x_4 + x_1^2 x_2^2 + x_1^4 x_2 + 2x_2 x_4 + x_2^3] \\ P_{C_i} &= \frac{1}{2} [x_1^6 + x_2^3]. \end{aligned}$$

The corresponding generating functions are shown below.

$$\begin{aligned} \text{G.F.}_{C_{4h}} &= \frac{1}{8} [(\alpha_1 + \alpha_2)^6 + 2(\alpha_1 + \alpha_2)^2 (\alpha_1^4 + \alpha_2^4) \\ & + (\alpha_1 + \alpha_2)^2 (\alpha_1^2 + \alpha_2^2)^2 + (\alpha_1 + \alpha_2)^4 (\alpha_1^2 + \alpha_2^2) \\ & + 2(\alpha_1^2 + \alpha_2^2) (\alpha_1^4 + \alpha_2^4) + (\alpha_1^2 + \alpha_2^2)^3] \\ \text{G.F.}_{C_i} &= \frac{1}{2} [(\alpha_1 + \alpha_2)^6 + (\alpha_1^2 + \alpha_2^2)^3]. \end{aligned}$$

The coefficient of $\alpha_1^5 \alpha_2$ in these generating functions are 2 and 3, indicating 2 and 3 equivalence classes under the action of C_{4h} and C_i symmetries. Thus a single fluorine NQR line for antiferroite crystal splits into two lines for a distorted crystal with C_{4h} symmetry and three lines for a crystal with C_i symmetry. In the next section we apply the double coset method described by Ruch et al. [13] to NQR spectra.

3. Double coset method for the prediction of intensity patterns for crystals undergoing phase transitions

For a system with n nuclei the complete group of permutations and permutation-inversion operations is the group $S_n \times I$ where $I = \{E, E^*\}$ and S_n consists of the $n!$ permutations of n objects. Consider the permutation-inversion representation of the point group G of the unit cell [11]. Let us define a label subgroup of $S_n \times I$ for the n -nuclei NQR problem as $(S_{n-1} \times S_1) \times I$. For any $s \in (S_n \times I)$ the set LsG is known as the double coset of L and G in $(S_n \times I)$. Two elements s_1 and s_2 in $(S_n \times I)$ are defined to be equivalent if they are in the same double coset. A set $S = \{s_1, s_2, \dots, s_j\}$ with $s_i \in S_n \times I$ is said to be a set of distinct representatives if

$$\bigcup_{i=1}^l Ls_i G = S_n \quad \text{and} \quad (Ls_i G) \cap (Ls_j G) = \emptyset \quad \text{if } i \neq j.$$

The number of elements in S is the number of equivalence classes of nuclei. Each $s_i \in S$ generates an equivalence class of nuclei by the recipe we will now describe. Each $s_j \in S_n$ can act on f_n (the map which maps all the nuclei to α_1 except the n th nuclei which is mapped to α_2)

$$s_j f_n(d_k) = f_n(s_j^{-1} d_k), \quad d_k \in D.$$

The map $s_j f_n$ gives one nucleus in the equivalence class (since $s_j f_n$ maps all but that nucleus to α_2). The other nuclei in this class can be obtained by applying the elements of G on $s_j f_n$. The number of elements in any double coset LsG is given by

$$|LsG| = \frac{|L||G|}{|sLs^{-1} \cap G|} = \frac{|L||G|}{|L \cap s^{-1}Gs|}.$$

Thus the number of elements in any double coset LsG can be obtained without having to actually construct the double coset. The number of elements in a double coset is not, in general, equal to the number of elements in the corresponding equivalence class of nuclei. In general, the number of nuclei in an equivalence class corresponding to the double coset LsG is given by

$$\begin{aligned} \frac{|LsG| \cdot n}{|S_n \times I|} &= \frac{|L||G|}{|L \cap s^{-1}Gs|} \cdot \frac{n}{2(n!)} \\ &= \frac{|G|}{|L \cap s^{-1}Gs|}. \end{aligned}$$

This formula is quite useful in finding the intensity ratios of NQR signals.

Let us illustrate the above procedure with an antiferroite crystal exhibiting distortion. Let G be the group C_{4h} . The permutation-inversion representation of C_{4h} is $\{E, (2345), (2543), (24)(35), (16)(24)(35)^*, (16)(2543)^*, (16)(2345)^*, (16)^*\}$. In this case the label subgroup L is $(S_5 \times S_1) \times I$. We already know from generating function methods that there are 2 equivalence classes of nuclei for C_{4h} . One obvious choice of a distinct representative is $s_1 = E$, the identity. The action of $s_1 = E$ on f_6 generates f_6 itself. Thus the nucleus 6 is a member of the equivalence class corresponding to s_1 . The only other element in this class is f_5 or the nucleus 5. This is obtained by applying the elements of G on this nucleus. s_2 can be seen to be (46). The permutation (46) was chosen since it is not present in LEG. s_2 generates f_4 on its action on f_6 . Elements of G generate the second equivalence class.

In practice for the analysis of NQR spectra we do not need to construct these double cosets and equivalence classes. We need only the number of nuclei in each equivalence class and the set of distinct representatives. For this purpose we use the formula that we outlined earlier. Thus the number of elements in the equivalence class corresponding to E , is

$$\frac{|G|}{|L \cap E^{-1}GE|} = \frac{|G|}{|L \cap G|} = \frac{8}{4} = 2.$$

Note that $L \cap G = \{E, (2345), (2543), (24)(35)\}$. Thus the other class obviously contains four elements. Consequently, the intensity ratio of these two NQR lines is 2:1.

Consequently, in order to analyze NQR spectra of crystals exhibiting distortion it is not necessary to know the character spanned by nuclei in various symmetries. Using double coset methods intensity patterns can be analyzed without having to construct the double cosets or equivalence classes.

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