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MAGNETIC RESONANCE AND THE PROBLEM OF THE DEFINITION OF ANTIFERROELECTRICITY

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Résumé. — Contrairement aux cas des ferroélectriques, l'attribution « antiferroélectrique » nécessite des données sur le cristal qui s'étendent au-delà du niveau macroscopique (groupe ponctuel). Comme illustré par l'exemple du péríode d'ammonium ces informations détaillées peuvent être obtenues par l'étude des interactions quadrupolaires. On souligne que la définition de l'antiferroélectricité doit être restreinte aux cristaux, dans lesquels des interactions électriques sont essentielles pour le mécanisme qui provoque la transition de phase.

Abstract. — In contrast to the case of ferroelectrics the assignment of antiferroelectricity presupposes information on the crystal which goes beyond the macroscopic (point group symmetry) level. Illustrated by the example of ammonium periodate these full data may be obtained by the study of nuclear quadrupole interactions. It is emphasized that the definition of antiferroelectricity has to be restricted to crystals, in which electric interactions are essential for the driving mechanism of the phase transition.

1. Introduction. — It is possible to identify a crystal as ferroelectric by the phenomenological (macroscopic) observation of a switchable or — more generally speaking — of a reorientable spontaneous polarization alone. By now it is well established that the knowledge of the point symmetry of the non-ferroelectric high temperature phase (also called parent or initial phase) and of the orientation of the spontaneous polarization is sufficient to determine the point symmetry of the ferroelectric phase (see review by Shuvalov [1]). The same macroscopic data are adequate for the assignment of the symmetry of the « soft » mode responsible for the ferroelectric transition, as shown recently by Lavrencic and Blinc [2]. Therefore, experiments which yield information at the atomistic (space group) level are not a necessity for assigning a crystal as ferroelectric. However, e.g. the investigation of the phonon dispersion is an important alternative in cases where no dielectric studies are possible as treated by Steigmeier earlier in this meeting [3].

The situation is quite different in antiferroelectricity. Kittel [4] who introduced the concept by analogy to antiferromagnetism postulated the existence of spontaneously polarized lines of ions with neighbouring lines polarized in antiparallel direction, so that no macroscopic spontaneous polarization of the crystal results. It is generally accepted that any definition of antiferroelectricity includes the requirement of an antipolar crystal structure. As already Känzig [5] had shown, an antipolar structure need not have a multiple elementary cell as compared to the parent phase, but no such cases seem to be known. Apart from this special situation where parent and antiferroelectric phase are possible in the same space group, the translation symmetry of the crystal changes at the antiferroelectric transition point. As a consequence, the knowledge of the point group and of purely macroscopic properties of the crystal is not sufficient to assign antiferroelectricity to a crystal phase.

2. Critical comment. — Before we start to discuss the virtues of nuclear quadrupole resonance investigations as means of obtaining information at the atomistic (space group) level, we have to point out that there is some controversy about the definition of antiferroelectricity. If the antipolar structure is the only prerequisite, then many crystals such as SrTiO₃ (below 105 K) qualify as antiferroelectric. These are cases with practically no anomaly of the dielectric behaviour at the phase transition. As the driving mechanism is a « soft » mode of rotational character, there is no essential interaction to electric fields (see discussion by Gränicher and Müller [6]). The present author had proposed in 1957 [7] that the use of the term antiferroelectric should be « restricted to cases, where the interaction is essentially of the same nature as in ferroelectrics ». Such an amendment to the definition of the antiferroelectric state has been formulated by Jona and Shirane [8] in terms of thermodynamics. They call an antipolar crystal antiferroelectric if its free energy is comparable to that of a polar crystal. Today this is best understood in terms of Cochran’s theory of distortive phase transitions. Kittel’s thermodynamic theory can be expressed by two lattice vibration modes with a strong temperature dependence of their frequencies (Cochran and Zia [9] and Zein et al. [10]). Experimental evidence for a ferro- and an antiferroelectric mode in PbZrO₃ has been given recently by Samara [11].

Without giving further details here, we emphasize
that the definition of antiferroelectricity in the restricted sense is adequate to the character of the mechanism driving the crystal into the antiferroelectric state.

3. The application of spin resonance to antiferroelectrics. — In antiferromagnetism the magnetic scattering of neutrons offers a unique tool to reveal the antipolar sublattice magnetization. Unfortunately there is no electric analogue to this method of investigation. Therefore, we turn to the question what evidence may be derived from spin resonance techniques. Here too, the magnetic case is easier to solve. A particularly straightforward and illuminating example is the study of Poulis and Hardeman [12] on CuCl₂·2H₂O. This crystal becomes antiferromagnetic below \( T_N = 4.37 \) °K. The protons are subject to the external magnetic field \( H_0 \) plus the local field produced by the antiparallel copper ion sublattice magnetizations. By taking a rotation pattern of the proton resonance lines, the field contributions due to the sublattices become directly apparent.

In the electric analogue it is possible to sense the electric field not directly but its gradient at the sites of nuclei with electric quadrupole moments. This looks like a disadvantage at first sight, but in suitable materials a wealth of information can be derived from NQR investigations. It is basic that the symmetry properties of the electric field gradient (E. F. G.) tensor are determined by the point symmetry at the site of the nuclei under study. In addition to sites which are related by the crystal symmetry (physically equivalent sites), there may be chemically inequivalent nuclear sites which e. g. show up when the crystal is cooled through the transition temperature.

Shimomura [13] argued that the Laue group of a crystal may be determined from the number of orientations of equivalent E. F. G. tensors. But his conclusion that the analysis of the N. Q. interaction does not offer more information than the Laue technique in X-ray scattering is not correct. An interesting example is the investigation of the so called « antiferroelectric » phase of ammonium periodate \((\text{NH}_4)_2\text{H}_3\text{IO}_6\) [14]. As the chemical formula and the room temperature structure of this material were known, the low temperature phase could be derived from \(^{1}^2^7\) resonance data in great details. An ambiguity between two allowed space groups remained. But similar studies on deuterated crystals will enable to decide between the two groups. The structure model obtained may be checked by a consistent calculation of all the observed E. F. G. tensor components.

All the information described above is derived from the resonance spectra. An additional and powerful source of information is the study of the temperature dependence of the spin-lattice relaxation time \( T_1 \) as presented at this meeting by A. Rigamonti [15].

References

[3] Steigmeier (E. F.), these proceedings.
[15] Bonera (G.), Borsa (F.) and Rigamonti (A.), these proceedings.