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To cite this version:

G. Czjzek. BOND-ANGLE DISTRIBUTION AND THE LOCAL FIELD ACTING ON RARE-EARTH IONS IN AMORPHOUS SOLIDS. Journal de Physique Colloques, 1985, 46 (C9), pp.C9-113-C9-121. <10.1051/jphyscol:1985914>. <jpa-00225280>

HAL Id: jpa-00225280
https://hal.archives-ouvertes.fr/jpa-00225280
Submitted on 1 Jan 1985

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BOND-ANGLE DISTRIBUTION AND THE LOCAL FIELD ACTING ON RARE-EARTH IONS IN AMORPHOUS SOLIDS

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Résumé - Des sondes locales dont les propriétés dépendent de la distribution des charges dans l'environnement peuvent rendre des informations sur la structure des amorphes qui sont alliées à la distribution des angles de liaison, un supplément important aux distributions radiales dérivées des mesures de diffraction. La relation entre les paramètres de structure et les quantités observables par expérience, comme la distribution des niveaux d'énergie et la susceptibilité magnétique, est élaboré en utilisant un formalisme qui permet l'évaluation des résultats expérimentaux sans supposition d'un modèle de la structure.

Abstract - Local probes whose properties depend upon the distribution of charges in their environment can provide structural information about amorphous solids which is related to bond angle distributions, an important supplement to radial distributions derived from diffraction techniques. The relation between structural parameters and experimentally observable quantities such as energy level distributions and magnetic susceptibilities is worked out in terms of a formalism which allows a model-free evaluation of the experimental results.

I - INTRODUCTION. LOCAL MULTIPOLe FIELDS

In the past few years, the techniques of diffraction measurements for the determination of amorphous structures have been refined enormously. They yield quite detailed information about partial pair correlation functions which are essential for our knowledge about chemical ordering in amorphous materials. In spite of this, fundamental questions concerning the topology of local atomic arrangements remain open. It has been pointed out by Hafner /1/ that a clarification of these problems cannot be achieved on the basis of radial pair correlation functions alone. Higher order correlation functions, as for example bond-angle distributions should be accessible to experimental investigation.

In this report, a preliminary account of an investigation of the use of local probes, mainly of rare earth ions, for the derivation of experimental information about higher order correlation functions related to bond-angle distributions is presented.

The state of an isolated probe - an ion or an atomic nucleus - is determined by some internal potential of spherical symmetry. Hence, the state is characterized by an angular momentum \( J \) (nuclear spin \( I \)). In a solid, the probe located at position \( \mathbf{r} \) is furthermore subject to an electrostatic potential which originates from all charges \( z_i \) at positions \( \mathbf{r}_i \) in the surroundings:
The task of determining the states of the probe under the action of 
(1) is most easily achieved by expansion of \(|\mathbf{r}_1 - \mathbf{r}_1|^{-1}\) in terms of spher- 
ical harmonics, and by introduction of operator equivalents using the 
Wigner-Eckhart theorem /2/. In this way, the expression for \(V_{LF}\) is 
transformed to

\[
V_{LF} = \sum_{k,q} B_k^q Q_k^q (k=1,2,\ldots; -k \leq q \leq k) 
\]

The quantities \(Q_k^q\) are operators ("multipole operators") in the angular 
momentum space of the local probe, with matrix elements /3/

\[
\langle J,M'|Q_k^q|J,M\rangle = \frac{1}{2^{k+1} \sqrt{2J+1}} \frac{1}{(2J-k)!} \frac{1}{(2J+k+1)!} \langle J,M,q|J,M'\rangle 
\]

where \(\langle J,k,M,q|J,M'\rangle\) are Clebsch-Gordan coefficients (notation as in 
A. Messiah /4/).

The local multipole field (LMF) parameters \(^1\) \(B_k^q\), in the notation 
customarily used for rare earth ions /2/ are given by

\[
B_k^q = \left(\frac{4\pi}{2k+1}\right)^{1/2} (1-\delta_k^q) e^{i k \cdot \mathbf{r}} \cdot \epsilon_j^{(k)} \cdot A_k^q 
\]

with

\[
A_k^q = \sum_{i} \frac{z_i}{r_i^{k+1}} \cdot \gamma_k^q (\theta_i, \phi_i) 
\]

For the meaning of the other factors in eq. (4), characterizing the 
probe ions, the reader is referred to the literature on crystal field 
effects, for example ref. /5/. For the Stevens factor \(\epsilon_j^{(k)}\), the usual 
notation is \(a_J, b_J, c_J\) for \(k = 2,4,6\), respectively.

The parameters \(A_k^q\) defined by the sums in eq. (5) are the quantities 
relevant for structural investigations. For ions embedded in a crys- 
tal lattice, each of them has the same precisely defined value for all 
equivalent lattice sites. In an amorphous solid, its value is again 
precisely defined for a given site, but variations in the local en-
vvironments from site to site lead to some probability distribution of 
these quantities for the ensemble of ions in the material studied. 
The relation between local structures, i.e. the distribution of charge 
positions in the environment of the probes, of the quantities \(A_k^q\), and 
of the resulting physical properties of the probe ions will be 
treated in the following sections.

Before turning to this principal subject of the report, however, some 
remarks concerning the particular choice of rare earth ions and nuclei 
as structural probes appear in place since the potential introduced

\(^1\) For ions in crystals, these are the crystal field parameters. 
Most authors transfer the name to amorphous solids. I prefer to 
avoid the expression "crystal" field when referring to amorphous 
materials.
in eq. (1) is quite universal, acting on any ion in a solid.

The selection is based on 2 conditions. Firstly, the probe must be well localized. If it were not, the extension of the region sampled would not be well defined. Actually, the transformation of eq. (1) to the expressions in eq. (2) through (5) would not be valid for extended probes. In addition, a localized probe has discrete energy levels corresponding to precisely defined states.

The condition of localization obviously is met by atomic nuclei, and it holds in general for the 4f electrons of rare earth ions unless we happen to meet a case of fluctuating valence.

The second condition concerns the ratio between the strength of the interaction with the environment, \( E_{\text{ext}} \), and the strength of internal interactions, \( E_{\text{int}} \), which are measured by the energy difference between the ground state and excited states of the isolated probe. Only if this ratio is significantly smaller than 1, the state resulting from the interaction with the external potential is described in a simple way by ground state properties of the probe such as radial moments. Otherwise, the final state contains admixtures of excited probe states, and a rather detailed knowledge of internal interactions is required for understanding the ensuing properties of the probes.

For nuclei, \( E_{\text{ext}} \) is typically a few times \( 10^{-6} \) eV whereas \( E_{\text{int}} \) amounts to \( 10^3 \) eV or more. Thus, this ratio is very small. For rare earth ions, although the situation is not quite as favourable, with \( E_{\text{ext}} \sim 10^{-2} \) eV, and \( E_{\text{int}} \) varying from about 0.2 eV for light rare earths to about 1 eV for heavy rare earths, the ratio is sufficiently small for the neglect of excited state admixtures to be a reasonable approximation.

Then, because of parity conservation, only even values of \( k \) have to be taken into account in eq. (2). For nuclei, only \( k = 2 \) leads to measurable effects. Higher terms escape detection because of the small spatial extent of the nuclear charge distribution. An investigation of the distribution of nuclear quadrupole interactions in amorphous solids has been described in ref. /6/.

Here, the approaches employed in ref. /6/ will be extended to the use of rare earth ions as structural probes in amorphous materials. For rare earth ions, the terms for \( k = 2, 4, \) and 6 have to be considered. This complicates the analysis, but at the same time it augments the information that can be extracted.

II - DISTRIBUTION OF THE LMF PARAMETERS, INVARIANT FUNCTIONS

The task of dealing with the distribution of all quantities \( A_k^q \) at first sight appears formidable, simply because of the large number of parameters. For each \( k \), there are \( (2k+1) \) parameters \( A_k^q \) for \( q \) running through the sequence \(-k,-k+1,\ldots,k\). For the 3 values of \( k \) to be considered for rare earth ions, this makes a total of 27 independent arguments of a general probability distribution \( P_A (\ldots A_k^q \ldots) \).

The problem was bypassed in the random anisotropy model /7/ by a severe truncation of the parameter set. Only the terms for \( k=2 \) were taken into account. The truncation was based on computer simulations
which had shown that for a structure corresponding to the model of dense random packing of hard spheres the effects of the terms for \( k=2 \) by far outweigh all others. The magnetic properties determined experimentally for several amorphous alloys were quite adequately described by this model /8/.

Since the approach of the random anisotropy model is based on a specific structural model, it is not suited for an unbiased investigation of amorphous structure. A model-independent alternative is proposed here. The only condition for its applicability is the isotropy on the average of the material under investigation.

This average isotropy is guaranteed for a large class of amorphous solids such as amorphous solids and semiconductors. In the case of classical window glasses, it is just this isotropy which makes them useful for optical instruments.

For an isotropic material, the distribution function \( P_A(\ldots A^q_k \ldots) \) must be independent of the choice of the coordinate system. It must be a scalar function, invariant under any rotation. Since the quantities \( A^q_k \) transform under rotations as the components of a tensor of \( k \)th order, the requirement of invariance restricts the form of the function \( P_A(\ldots A^q_k \ldots) \).

Elementary invariant functions of the quantities \( A^q_k \) can be constructed by the rules of coupling of angular momenta. These functions are homogeneous forms in \( A^q_k \) of degree \( N = 2, 3, \ldots \). Some simple examples are:

\[
S_2(k) = \sum_{q} (-1)^q A^q_k \cdot A^{-q}_k
\]

\[
S_3(k_1, k_2, k_3) = \sum_{q_1, q_2} (-1)^{q_1+q_2} \langle k_1, k_2, q_1, q_2 | k_3, q_1+q_2 \rangle x k_1 \cdot k_2 \cdot k_3
\]

The invariance of the function \( P_A(\ldots A^q_k \ldots) \) implies that it can be expressed in terms of the invariant functions \( S_N \):

\[
P_A(\ldots A^q_k \ldots) = P_S[S_2(2), S_2(4), S_2(6), S_3(2, 2, 2), \ldots]
\]

By substitution of eq. (5) into the equations (6), the functions \( S_N \) can be expressed in terms of the coordinates of the charges causing the local fields. In accordance with the invariance of \( S_N \), these expressions can be transformed to functions of radial distances \( r_i \) and of bond angles \( \theta_{ij} \) where \( \cos \theta_{ij} = \cos \theta_i \cdot \cos \theta_j + \sin \theta_i \cdot \sin \theta_j \cdot \cos (\phi_i - \phi_j) \).

For \( N = 2 \), the addition theorem of spherical harmonics yields directly...
For $N=3$, the calculation is somewhat more tedious. I quote some results using the abbreviations $y_{ij} = \cos \theta_{ij}$, and $\Sigma^*$ to indicate sums over 3 indices from which all terms with 2 or 3 equal index values are omitted.

$$S_3(2,2,2) = \Sigma^* \frac{z_{ij} z_{jk} z_{kl}}{i j k r_i r_j r_k} \left[ 9y_{ij} y_{ij} y_{jk} - 3(y_{ij}^2 + y_{ij} y_{jk}^2) + 2 \right]$$

$$+ \frac{1}{2} \Sigma^* \frac{z_{ij} z_{jk} z_{kl}}{i j k r_i r_j r_k} \left[ \frac{z_i}{r_i} \frac{z_j}{r_j} + \frac{z_k}{r_k} \right] (3y_{ij}^2 - 1) + \frac{1}{2} \Sigma^* \frac{z_i^2}{r_i}$$

$$S_3(2,2,4) = \frac{1}{8} \Sigma^* \frac{z_{ij} z_{jk} z_{kl}}{i j k r_i r_j r_k} \left[ 35y_{ij}^2 y_{ij}^2 - 20y_{ij} y_{jk} y_{kl} - 5(y_{ij}^2 + y_{jk}^2) \right]$$

$$+ \frac{1}{8} \Sigma^* \frac{z_{ij}^2 z_{jk}^2}{i j k r_i r_j r_k} \left[ 35y_{ij}^4 - 30y_{ij}^2 + 3 \right] + \frac{1}{8} \Sigma^* \frac{z_{ij}^2 z_{jk}^2}{i j k r_i r_j r_k} \left[ 3y_{ij}^2 - 1 \right] + \frac{1}{8} \Sigma^* \frac{z_i^3}{r_i}$$

The details of these expressions are not of special importance. However, the expressions shown illustrate that the degree $N$ of the invariant functions $S_N$ is an indicator of the level of correlation involved in the probability distribution $P_S(S_N)$. If the central ion as origin of the local coordinate system is taken into account, the level of correlation is $(N+1)$. Thus, the distribution functions $P_S(S_2)$ involve triple correlations, similar to the bond-angle distribution $f(\theta_{ij})$ defined by Hafner /1/. $P_S(S_3)$ involves quadruple correlations, etc.

This result gives an important clue for a simplification in handling the large number of arguments in the general distribution function. For a crystal, all functions $S_N(k_1, k_2, \ldots)$ have some precisely defined value, that is

$$P_S^{\text{Cryst}} (\ldots, S_N, \ldots) = \pi \sum_{N, k_1} \delta(S_N(k_1, k_2, \ldots) - S_N^{\text{Cryst}}(k_1, k_2, \ldots))$$

If disorder is introduced gradually, the sharp delta functions become smeared out, and the broadening may be expected to proceed the faster, the higher the level of correlation. For strong disorder, a significant structure will be found only in the dependence of $P_S$ upon the arguments $S_N$ with small values $N$.

On the opposite extreme, for "ideal" disorder, general arguments as used in ref. /6/, indeed lead to a probability distribution which depends upon $S_2(k)$ only:
Of course, the conditions underlying the derivation of eq. (8) correspond to those found in a gas rather than in a densely packed solid.

For the distribution of electric field gradients, that is, for LFM parameters with \( k = 2 \) only, the distribution for dense random packing was shown in ref. \(/6/\) to be only slightly modified compared to that given in eq. (8). It is very well approximated by

\[
P^S_{\text{DRP}} = [1 + \beta \cdot S_3(2,2,2) / \sigma^2_2] \cdot P^G_S[S_2(2)]
\]

with \( |\beta| \sim 10^{-2} \)

For structural studies of amorphous solids in general, information about triple and quadruple correlation functions corresponding to probability distributions of \( S_2(k) \) and of \( S_3(k_1,k_2,k_3) \) will be of primary interest.

III - PHYSICAL PROPERTIES OF AMORPHOUS SOLIDS CONTAINING RARE EARTH IONS

The local potential \( V_{\text{LF}} \) acting on the 4f shell leads to a partial lifting of the \((2j+1)\)-fold degeneracy of the ionic ground state. Along with the variations of the LFM parameters \( B^k \), this results in a distribution of energy splittings for the ensemble of rare earth ions. The distribution of energy splittings can be determined experimentally by inelastic neutron scattering /9/ and by measurements of the specific heat /10/.

Furthermore, the magnetic moments of the 4f states, the field dependence of the magnetization, and the temperature dependence of the magnetic susceptibility are sensitive indicators of the local fields /11,12/.

Finally, electron spin resonance spectra and the hyperfine interactions of the 4f electrons with the nuclei of the probe ions can be employed in testing the distribution of local fields acting on the rare earth ions /13,14/.

All experimental investigations quoted were evaluated in terms of the random anisotropy model /7/, of a slightly extended version /15/, or in comparison with the distribution derived in ref. /6/ for the terms \( B^k \). In most cases, deviations from the results expected for a dense random packing structure were found. Two independent studies of amorphous Ce-Al alloys /10,12/ yielded evidence for important effects of higher-order \((k=4,6)\) local fields.

The approach described in the previous section, employing invariant functions of the LFM parameters, provides the possibility for a more general analysis of experimental data. The quantities observable by experiments can be expressed in terms of the invariant functions \( S^N \). Here, I will demonstrate this for distributions of energy levels and for the magnetic susceptibility.

1 - Energy Level Distributions

The energy levels of an ion under the action of the local potential \( V_{\text{LF}} \) are the solutions of the secular equation

\[
P^S = \exp[-\sum_{k} S_2(k)/2\sigma^2_k]
\]

(8)
For given $J$, eq. (10) is a polynomial equation in $E$ of power $(2J+1)$, the coefficients of the polynomials being linear combinations of the invariant functions $S_N$ defined in section II. Some simple examples are:

$J = 1$:

$$E^3 - \frac{3}{4} S_2(2,2) E - \frac{1}{4} S_3(2,2,2) = 0$$

$J = \frac{3}{2}$:

$$E^2 - \frac{9}{4} S_2(2,2) = 0$$

$J = \frac{5}{2}$:

$$E^3 - [21S_2(2,2) + \frac{1575}{4} S_2(4,4)] E$$

$$- 20S_3(2,2,2) - 465S_3(2,2,4) + 1125S_3(2,4,4) + \frac{10125}{4} S_3(4,4,4) = 0$$

The general form is:

$$E^{2J+1} - C_2 E^{2J-1} + C_3 E^{2J-2} \ldots = 0$$

with

$$C_2 = \frac{1}{2} \sum_{\lambda} \frac{E_\lambda^2}{E_\lambda} = \sum_k a_k S_2(k)$$

$$C_3 = \frac{1}{3} \sum_{\lambda} \frac{E_\lambda^3}{E_\lambda} = \sum_{k_1,k_2,k_3} \beta_{k_1,k_2,k_3} S_3(k_1,k_2,k_3)$$

Since the coefficients $C_n$ of the energy polynomial (11) are linear functions of $S_N$, the probability distribution $P_C(\ldots C_n \ldots)$ is easily derived from the distribution $P_S(\ldots S_n \ldots)$, and from standard algebra the distribution function of the energy levels $E_\lambda$ follows as

$$P_E(\ldots E_\lambda \ldots) = P_C(C_2 = \frac{1}{2} \sum_{\lambda} E_\lambda^2, C_3 = \frac{1}{3} \sum_{\lambda} E_\lambda^3, \ldots) \delta(\sum_{\lambda} E_\lambda) \prod_{\lambda < \mu} |E_\lambda - E_\mu|$$

For the large values of $J$ encountered for most rare earth ions, the expressions become too lengthy for analytical calculations to be reasonable. The procedure outlined here, however, is easily applied for computer calculations.

Eq. (13) can be used in evaluating specific heat data. For inelastic neutron spectroscopy, a modification is necessary since the observed intensities involve matrix elements for transitions between eigenstates of the local-field Hamiltonian.
Magnetic Susceptibility

The response of rare earth probe ions to an applied magnetic field $\vec{H}$ is treated along similar lines. I assume a diluted alloy with negligible exchange interactions between magnetic ions. Only the interaction with the applied field is then added to the local-field Hamiltonian: $H = V_{JF} - g_J \mu_B \vec{H} \cdot \vec{H}$. The solutions $E_\lambda(H)$ of the secular equation depend upon the applied field. The magnetization $\vec{M}_\lambda(H)$ for state $\lambda$ is given by

$$E_\lambda(H) - E_\lambda(0) = -\vec{M}_\lambda(H) \cdot \vec{H}$$

and in the limit $\vec{H} \to 0$, we have $\vec{M}_\lambda = \chi_\lambda \cdot \vec{H}$.

For the bulk susceptibility considered here, the angular distribution of the local coordinate systems with respect to the direction of the applied field must be taken into account. In the case of an isotropic solid as it is assumed here, the average over a random distribution of orientations is appropriate.

The procedure is most easily outlined by a specific example. For $J=1$, the secular equation becomes with the abbreviation $\vec{h} = g_J \mu_B \vec{H}$:

$$E^3 - \frac{3}{4} S_2(2,2) + h^2 E_3(2,2,2) + h \cdot \vec{B} \cdot \vec{h} = 0 \quad (14)$$

The isotropic average over the last term is

$$<\vec{h} \cdot \vec{B}_2 \cdot \vec{h}> \text{ isotr} = \frac{1}{3} h^2 \cdot \text{Tr} \, \vec{B}_2 = 0$$

since $\text{Tr}(\vec{B}_2) = 0$. For larger $J$, similar terms occur with tensors formed by products of terms $B^2$. Then, the trace yields one of the invariant functions $S_N$.

For the calculation of the susceptibility in the limit $\vec{H} \to 0$, the expansion $E_\lambda(h) = E_\lambda(0) + h$ is substituted in eq. (14), and only terms linear in $\vec{h}$ are considered. This gives

$$\chi_\lambda = \frac{1}{3} g_J^2 \mu_B^2 E_\lambda(0) [E_\lambda(0) - \frac{1}{4} S_2(2)]$$

and for the bulk susceptibility one obtains

$$\chi(T) = <\chi_\lambda>_{\text{config}}$$

$$= \int \int \int dE_1 dE_2 dE_3 P_\Sigma(E_1, E_2, E_3) \cdot \sum_\lambda \chi_\lambda e^{-E_\lambda/k_BT} / \sum_\lambda e^{-E_\lambda/k_BT}$$

Thus, the temperature dependence of the magnetic susceptibility is related to the distribution of energy levels which in turn is determined by the distribution of local fields.

IV - SUMMARY AND OUTLOOK

The work presented here is still in progress, far from being completed. Thus, it appears premature to end this report by "conclusions". Firstly, the formalism outlined here must be elaborated for realistic calculations for the large $J$ values of rare earth ions. Special attention must be devoted to the shielding factors $\sigma_k$ appearing in eq. (4) which reflect the response of local closed electronic shells to lattice
potentials. They may have considerable values, differing for different \( k /5 \). Thus, in contrast to EFG distributions where \((1-\sigma_2)\) just is a scale factor \( /6 \), the contributions of different multipole orders to the LMF distributions are weighted differently depending upon the values of \( \sigma_k \), and hence the shape of the distribution functions is modified. For metallic materials, contributions of conduction electrons still present an unsolved problem. These questions will have to be worked out in connexion with experimental data for specific systems.

I hope to have given evidence, however, that rare earth ions can be considered as useful probes for studying the structure of amorphous solids, that they can yield information beyond radial distribution functions extracted from diffraction data. The most significant results can be expected from spectroscopic methods: inelastic neutron scattering, electron spin resonance, NMR, and Mössbauer spectroscopy, as in these the experimental data actually reflect the distribution function whereas results of bulk measurements are determined by some integrals averaging over the distribution.

ACKNOWLEDGEMENT

Large parts of the work described here were performed while I enjoyed the generous hospitality of the Department de Recherche Fondamentale at the Centre d'Etudes Nucléaires in Grenoble, and of the Laboratoire de Spectrométrie Physique at the University of Grenoble. My particular thanks go to my personal hosts, M. Bogé and J. Chappert at the Centre d'Etudes Nucléaires, and to C. Meyer and F. Hartmann-Boutron at the University.

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