

phys. stat. sol. (b) **120**, 745 (1983)

Subject classification: 19; 22.8.1

*Laboratory of Inorganic Chemistry and Materials Science,
Twente University of Technology, Enschede¹⁾*

The Interpretation of Broadened Gd³⁺ EPR Spectra of Polycrystalline Ceramics

By

H. J. A. KOOPMANS, M. M. A. PERIK, B. NIEUWENHUIJSE, and P. J. GELLINGS

An interpretation is given of the broadened EPR spectra of Gd³⁺ ions, which are frequently observed in polycrystalline ceramics and glasses. A reasonable simulation of the spectra is obtained, when these are regarded as a superposition of a large number of normal EPR powder spectra, each of which can be described with the usual spin-Hamiltonian. These originate from the many different surroundings of the Gd³⁺ ions in these compounds due to the structural disorder. The result is, that only those transitions, which are independent of the zero field splitting parameters in the spin Hamiltonian, remain visible in the derivative spectrum. The interpretation is supported by the EPR powder spectrum of the Gd³⁺ doped compound Ca.Hf₄O₉, which changes from broadened into clearly resolved, when the compound is ordered by an annealing process.

Eine Interpretation wird für die verbreiterten EPR-Spektren von Gd³⁺-Ionen gegeben, die häufig in polykristalliner Keramik und Gläsern beobachtet werden. Eine ziemlich gute Simulation dieser Spektren wird erhalten, wenn diese Spektren als Summe einer großen Anzahl normaler EPR-Spektren betrachtet werden, welche mit dem üblichen Spin-Hamiltonoperator beschrieben werden können. Die normalen Spektren werden von den vielen verschiedenen Umgebungen der Gd³⁺-Ionen verursacht, als Folge der strukturellen Unordnung in diesen Verbindungen. Das Ergebnis ist, daß nur solche Resonanzen wahrnehmbar sind im abgeleiteten Spektrum, die unabhängig von den Parametern der Nullfeldaufspaltung im Spin-Hamiltonoperator sind. Diese Interpretation wird durch das Verhalten des EPR-Spektrums eines Polykristalls der Gd³⁺-dotierten Verbindung Ca.Hf₄O₉ gestützt. Das erst verbreiterte Spektrum ändert sich in ein deutlich aufgespaltenes Spektrum, wenn die Verbindung in einem Temperungsprozeß geordnet wird.

1. Introduction

At this laboratory the relation between the microstructure and the electric properties of ferroelectric ceramics such as Pb_{1-1.5x}La_xZr_{1-y}Ti_yO₃ (PLZT) has been studied [1]. These materials all belong to the perovskite family ABO₃ (Fig. 1) and show a paraelectric-ferroelectric phase transition in conjunction with a structural phase transition. To explain the lowering of the phase transition temperature with increasing amounts of La³⁺ ions, these perovskites have been examined also by means of the EPR technique [2]. For that purpose a small percentage of the Pb²⁺ or La³⁺ ions was replaced by Gd³⁺. The observed EPR powder spectra of these samples with $x = 0$ and $y > 0.8$ (PZT) or with $x < 0.16$ and $y = 1$ (PLT) have been explained successfully in terms of the zero field splitting parameters B_n^m by the usual spin Hamiltonian

$$\mathcal{H} = \beta H g \hat{S} + \sum_{n=2,4,6} \sum_{m=-n}^{+n} B_n^m \hat{O}_n^m, \quad (1)$$

where \hat{O}_n^m are the Stevens operators [3, 4]. However, with increasing x or decreasing y , respectively, an increase of the linewidth is observed with respect to the EPR powder spectrum of Gd³⁺-doped PbTiO₃ [2]. Eventually this effect results in rather featureless

¹⁾ P.O. Box 217, 7500 AE Enschede, The Netherlands.

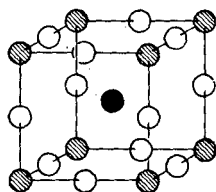


Fig. 1. Perovskite structure ABO_3 . ● A, ○ O, hatched circles B

X-band powder spectra for the other PLZT materials. These spectra show a large line-broadening together with some sharp lines at $g_{\text{eff}} \approx 2$ and ≈ 6 , where $g_{\text{eff}} = hv/\beta H$. It is found that these powder spectra are not at all characteristic of Gd^{3+} -doped PLZT materials. The same spectra of Gd^{3+} ions have been observed in many other compounds at this laboratory, as long as there exists some disorder in the lattice (e.g. vacancies, random distribution of ions, etc.). They are also observed in glasses containing Gd^{3+} ions [5, 6]. Recently Čugunov and Kliava [7] have attributed this powder spectrum to a superposition of a spectrum due to a rather well defined site of the Gd^{3+} ions with rhombic or lower symmetry ($g_{\text{eff}} \approx 6$) and a broad Gaussian line arising from clusters of Gd^{3+} ions ($g_{\text{eff}} \approx 2$). However, they did not explain, why there would be two totally different paramagnetic sites and why the line at $g_{\text{eff}} \approx 6$ disappears as the frequency is increased [6]. Although it might be possible that the Gd^{3+} ions can form their own environment in glasses, this is not very likely in the PLZT materials, where the overall structure is well defined. Moreover, the above-mentioned frequency dependence of the powder spectrum is also found in the temperature dependence of the X-band spectra of the PLZT ceramics (see [2], Fig. 2), when the structure changes from tetragonal to cubic. This confirms that the observed powder spectrum is still related with the overall structure.

In this research the broadened EPR powder spectrum is simulated on the basis of the assumption, that the Gd^{3+} ions are present in a large number of different surroundings. These are due to the random distribution of the Pb^{2+} and La^{3+} ions and vacancies over the A positions and of the Zr^{4+} and Ti^{4+} ions over the B positions in the case of the PLZT perovskites. Then the broadened powder spectrum is a superposition of a large number of spectra, each of which can be described separately by (1), but with different B_n^m -parameters. Moreover, if this assumption is correct, the broadened EPR powder spectrum will split into several clear resonances, if it is possible to order the compound. A few of such compounds have been examined. In some of these the order-disorder phenomena have also been studied by Raman spectroscopy [8].

2. Theoretical Considerations

To obtain an exact simulation of the observed powder spectrum on the above described basis, it is necessary to calculate a large number of EPR powder spectra, each of which is defined by a different set of B_n^m -parameters. However, this is rather time-consuming, if not completely impossible. Therefore, the following procedure has been used to limit the calculations. A literature survey [9] has shown that the most important zero field splitting parameters are B_2^0 and B_2^2 except for cubic EPR spectra. However, as stated by Čugunov and Kliava [7], it is not possible to explain the broadened spectrum on the basis of a cubic splitting, because such large splittings giving rise to the line at $g_{\text{eff}} \approx 6$ have never been found in a cubic environment. Although in principle it is not correct, a further simplification is made by assuming that B_2^2 is also zero. This means that for convenience only axial spectra are considered hereafter, because the simulation of axial powder spectra is rather easy in comparison with the non-axial case [2, 10]. Thus, the broadened EPR powder spectrum is regarded as the sum of a large number of spectra, which differ only in the B_2^0 -parameter.

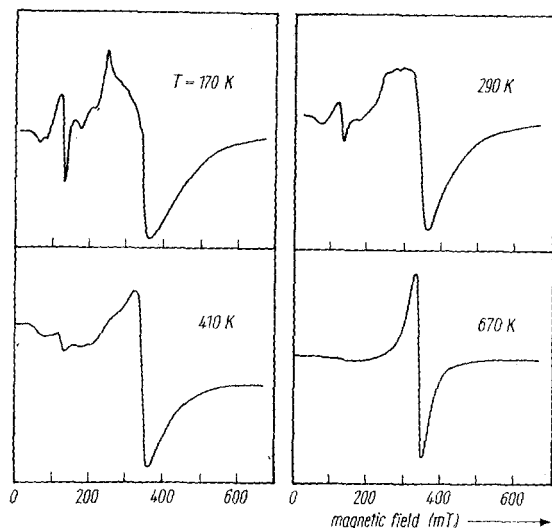


Fig. 2. X-band EPR powder spectra of Gd^{3+} -doped PLZT ($x = 0.12$ and $y = 0.45$) as a function of temperature (frequency 9.1 GHz)

It is clear from the temperature behaviour of the powder spectra of the PLZT materials, that there exists some distribution of these different B_2^0 -parameters. Fig. 2 shows that at $T = 670$ K most Gd^{3+} ions are present in a cubic environment. The mean B_2^0 -value will be about zero at this temperature. With decreasing temperature the absolute value of the average B_2^0 -parameter increases. If energetically there is no preference for a specific site, it is expected that the distribution of the ions over the different positions is statistically determined. Therefore, it is assumed that the distribution of the corresponding B_2^0 -values can be described by a Gaussian function. Such a function is defined by a mean B_2^0 -value ($\overline{B_2^0}$) and a spread in the B_2^0 -values (ΔB_2^0). Even with this simplified model a lot of computation time and core memory will be needed for a simulation. Therefore, the broadened EPR powder spectrum is approximated by the calculation of only one powder spectrum by means of (1) with $B_2^0 = \overline{B_2^0}$. To account for the distribution in B_2^0 -values, a Gaussian linewidth, which is proportional to dH_r/dB_2^0 , is allotted to each resonance H_r . Because the total intensity of each resonance has to remain constant irrespective of the attributed linewidth, the calculated intensity has to be taken inversely proportional to that linewidth [11]. It follows that only those resonances are visible in the simulation, which are almost independent of the B_2^0 -parameter. Other resonances are broadened too much and will not be visible in the derivate EPR powder spectrum.

3. Results

From the simulation of axial EPR powder spectra it is known that the probability to find a resonance between the magnetic field values H and $H + \Delta H$ is proportional to $\sin \theta$, where θ is the angle between the magnetic field vector and the principal axis of symmetry, usually designated as the z -axis [11]. Thus, the largest absorption is expected, when the magnetic field is oriented perpendicular to that z -axis. Therefore, it is reasonable to calculate the dependence of the b_2^0 -parameter²⁾ for the transitions of an $S = \frac{7}{2}$ system at this orientation firstly. The resonances and corresponding transition

²⁾ Proportionality factors have been used in these parameters, $b_2^0 = 3B_2^0$, $b_4^0 = 60B_4^0$, and $b_6^0 = 1260B_6^0$.

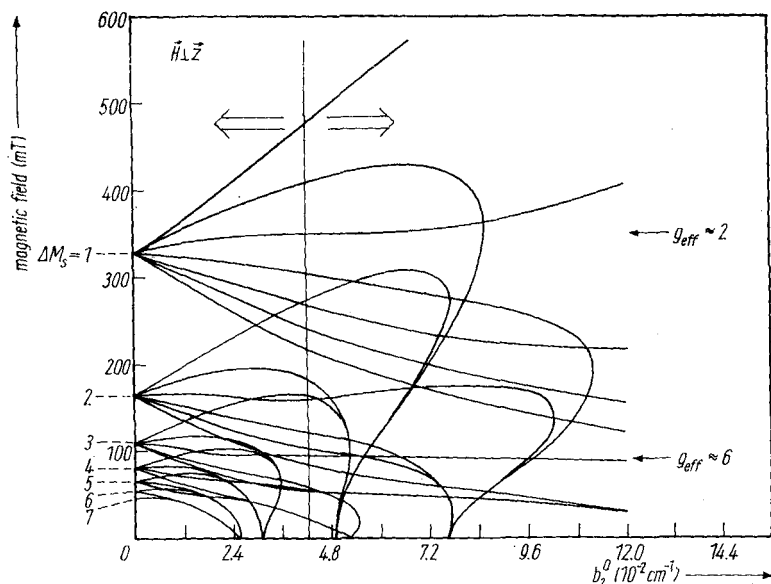


Fig. 3. Calculated transitions as a function of the zero field splitting parameter b_2^0 at constant frequency ($b_2^0 = 3B_2^0$). The direction of the magnetic field is perpendicular to the crystal z -axis ($S = \frac{7}{2}$, $g = 1.992$, frequency 9.1 GHz)

probabilities have been calculated with the program EPRALL, described by Heilbron [2]. The g -value of the Zeeman term in (1) has been taken equal to 1.992, because only in rare cases deviations are found from this value [9]. All calculations have been performed on a DEC-10 computer with a central core of 256 K-words of 35 bits. From Fig. 3 it can be seen that the lines at $g_{\text{eff}} \approx 2$ and ≈ 6 can be attributed to the marked transitions, because both are almost independent of the b_2^0 -parameter. Unfortunately, the transition probability is zero for the line at $g_{\text{eff}} \approx 6$ at this orientation. However, this is not the case for angles close to 90° and due to the fact that dH_r/db_2^0 is almost zero at these orientations too, its contribution to the powder spectrum can still be significant.

From Fig. 3 it is clear that the best mean \bar{b}_2^0 -value of the distribution is about $4.2 \times 10^{-2} \text{ cm}^{-1}$, because at that value dH_r/db_2^0 is also zero for the transition at $g_{\text{eff}} \approx 2$. For this b_2^0 -value a simulation of the broadened EPR powder spectrum has been performed. Except for the variable linewidths, the same procedure for the simulation has been followed as described by Heilbron [2]. Fig. 4 shows the result of the

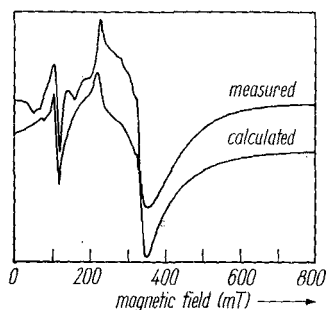


Fig. 4. Experimental and calculated X-band EPR powder spectra of Gd^{3+} -doped PLZT ($x = 0.12$ and $y = 0.45$) at $T = 170 \text{ K}$. The values $\bar{b}_2^0 = \Delta b_2^0 = 4.2 \times 10^{-2} \text{ cm}^{-1}$ have been used for the simulation (frequency 9.1 GHz)

simulation, which has been obtained by calculating the linewidth for each resonance with $\Delta b_2^0 = 4.2 \times 10^{-2} \text{ cm}^{-1}$. The resemblance is quite reasonable for this value. Note that values are included in the spin Hamiltonian for $b_4^0 (= 4 \times 10^{-4} \text{ cm}^{-1})$ and $b_6^0 (= 1 \times 10^{-4} \text{ cm}^{-1})$. This is merely done, because they are always present in the spin Hamiltonian and should be regarded as a mean value taken from the literature. However, they have no substantial contribution to the simulation, because the splitting of the resonances due to these parameters is very small.

The success of the simulation indicates that the lines at $g_{\text{eff}} \approx 2$ and ≈ 6 are correctly assigned. Although all orientations of θ between 0 and 90° are included in the calculation, no other directions are found, which gave a pronounced contribution to the simulation, either because θ is too small or dH_r/db_2^0 is too large. Thus, the simulation supports the idea that the broadened spectrum is due to disorder in the compounds. Therefore, several oxidic compounds, for which it was known that the ordering could be varied, have been investigated. All samples were synthesized as indicated in the cited literature. The most promising example of such a compound seemed to be the perovskite $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$, which can be synthesized in a disordered as well as a completely ordered form [12]. However, it was not possible to prevent the formation of a pyrochlore phase, which did not show any ordering. By changing the concentration of the Gd³⁺ ions it could be proven, that these ions initiated the formation of this phase. Several other systems, in which the order-disorder phenomena have been studied by means of Raman spectroscopy [8], have been investigated, too. However, no splitting of the broadened EPR powder spectra has been observed in most cases, because no significant order is obtained as e.g. in $\text{Y}_4\text{Zr}_3\text{O}_{12}$ [13]. Only CaHf_4O_9 shows the desired behaviour. The ordering process has been followed in this compound both by the EPR technique (Fig. 5) and by X-ray diffraction. As described by Delamarre [14] several order-

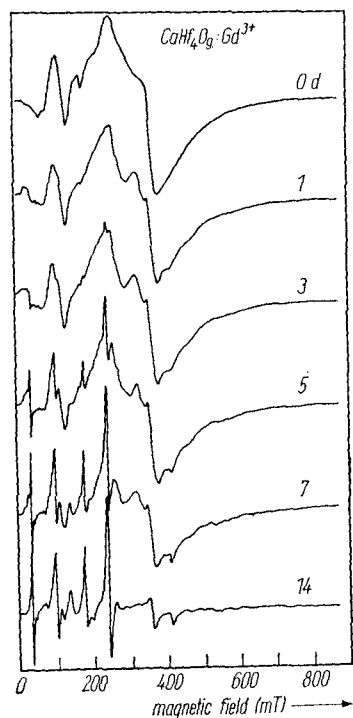


Fig. 5. The ordering process in CaHf_4O_9 doped with Gd^{3+} by annealing for several days at 1350 °C as studied by EPR (frequency 9.51 GHz)

ed phases can be obtained in this compound indicated by Φ , Φ_1 , and Φ_2 , depending on the annealing temperature. According to the detailed structural reports of Allpress and coworkers [15, 16] in fact the compound $\text{Ca}_2\text{Hf}_7\text{O}_{16}$ (Φ -phase) has been obtained together with small amounts of other phases. The powder spectrum observed after annealing two weeks (Fig. 5) resembles in many respects the one observed for Gd^{3+} -doped La_2O_3 . Measurements of Gd^{3+} -doped La_2O_3 single crystals have revealed a very large splitting in this compound, $b_2^0 = 13.1 \times 10^{-2} \text{ cm}^{-1}$ [17]. Although it is frequently reported that an ordering process of this kind also occurs in CaZr_4O_9 by annealing at 1000°C [18, 19], ordering was found neither with X-ray diffraction nor with EPR experiments. Recently Hellmann and Stubican [20] have published that the ordering temperature should be as high as 1180°C and no Φ -phase was detected. Due to the long annealing time needed for complete ordering (5 months), this compound has not been examined extensively at this laboratory. However, some preliminary experiments have shown the results of these authors to be correct.

4. Discussion

Although some features of the broadened EPR powder spectrum are correctly predicted by the simulation, it should be kept in mind that the procedure followed here is only an approximation. Because the transitions and corresponding transition probabilities are calculated from only one b_2^0 -value, it cannot be expected that all features of the observed powder spectrum can be explained in this way. However, it is clear that only those resonances are visible, which are independent of the b_2^0 -parameter. Therefore, the real distribution of the b_2^0 -parameters remains obscure and the choice of a Gaussian distribution has not necessarily to be correct. In this sense the mean b_2^0 -value of $4.2 \times 10^{-2} \text{ cm}^{-1}$ should not be seen as characteristic of the most occurring site of the Gd^{3+} ion, but merely as a proper choice for the simulation. From the fact that most transitions are broadened, it is obvious that the spread in the b_2^0 -values is large. However, the calculated spread in the b_2^0 -values should be seen as an indication, especially because the dependence of the b_2^0 -parameter is neglected. Unfortunately, the transitions attributed to the lines at $g_{\text{eff}} \approx 6$ and ≈ 2 are not independent of this parameter. Therefore, the spread in b_2^0 -values might be smaller, although the very large b_2^0 -value found for $\text{Ca}_2\text{Hf}_7\text{O}_{16}$ should also be taken into account.

Nevertheless the assignment of the broadened EPR powder spectrum to a superposition of a large number of well-defined spectra explains all the observations. The disappearance of the line at $g_{\text{eff}} \approx 6$ with increasing frequency is due to the fact that this is a "forbidden" transition with low transition probability. If the Zeeman term of (1) is large with respect to the crystal field term, then the transition probability reduces to zero. The same effect is observed in the temperature dependence of the spectra of the PLZT materials, where the overall structure transforms from tetragonal to cubic ($b_2^0 \rightarrow 0$). Moreover the idea is clearly supported by the change from a broadened EPR spectrum to a resolved one, when the compound CaHf_4O_9 is ordered by annealing. The suggestion that there exists a limited number of well defined sites for the Gd^{3+} ions, as frequently made for glasses, should be rejected. The observed features in the broadened EPR powder spectrum are due to resonances, which are independent of the b_2^0 -parameter. Therefore, no conclusions can be drawn about the sites of the Gd^{3+} ions. On the other hand, this effect explains adequately the observation of the same broadened EPR powder spectra of the Gd^{3+} ions in so many totally different host compounds.

References

- [1] C. G. F. STENGER and A. J. BURGGRAAF, *J. Phys. Chem. Solids* **41**, 17, 25, 31 (1980).
- [2] M. A. HEILBRON, Ph. D. Thesis, Enschede (The Netherlands) (1977).
- [3] A. ABRAGAM and B. BLEANY, *Electron Paramagnetic Resonance of Transition Ions*, Oxford Univ. Press, London 1970.

- [4] K. W. H. STEVENS, Proc. Phys. Soc. **A65**, 209 (1952).
- [5] I. V. CHEPELEVA and V. N. LAZUKIN, Dokl. Akad. Nauk SSSR **226**, 311 (1976).
- [6] R. C. NICKLIN, J. K. JOHNSTONE, R. G. BARNES, and D. R. WILDER, J. chem. Phys. **59**, 1652 (1973).
- [7] L. ČUGUNOV and J. KLIAVA, J. Phys. C **15**, L933 (1982).
- [8] D. MICHEL, M. PEREZ y JORBA, and R. COLLONGUES, J. Raman Spectroscopy **5**, 163 (1976).
- [9] H. A. BUCKMASTER and Y. H. SHING, phys. stat. sol. (a) **12**, 325 (1972).
- [10] H. J. A. KOOPMANS, B. NIEUWENHUIJSE, and P. J. GELLINGS, submitted to J. magnetic Resonance.
- [11] J. E. WERTZ and J. R. BOLTON, Electron Spin Resonance, McGraw-Hill Publ. Co., New York 1972.
- [12] C. G. F. STENGER, F. L. SCHOLTEN, and A. J. BURGGRAAF, Solid State Commun. **32**, 989 (1979).
- [13] S. P. RAY, V. S. STUBICAN, and D. E. COX, Mater. Res. Bull. **15**, 1419 (1980).
- [14] C. DELAMARRE, Rev. Internat. Hautes Températures Réfractaire **9**, 209 (1972).
- [15] J. G. ALLPRESS, H. J. ROSSELL, and H. G. SCOTT, Mater. Res. Bull. **9**, 455 (1974).
- [16] H. J. ROSSELL and H. G. SCOTT, J. Solid State Chem. **13**, 345 (1975).
- [17] D. VIVIEN, A. KAHN, A. M. LEJUS, and J. LIVAGE, phys. stat. sol. (b) **73**, 593 (1976).
- [18] G. BACQUET, J. DUGAS, C. ESCRIBE, and F. FABRE, C.R. Acad. Sci. (France) **276B**, 47 (1973).
- [19] D. MICHEL, Mater. Res. Bull. **8**, 943 (1973).
- [20] J. R. HELLMANN and V. S. STUBICAN, Mater. Res. Bull. **17**, 459 (1982).

(Received August 29, 1983)