

Creative

Color Centers and Jahn-Teller Effect in Ionic Crystals—My Scientific Encounters with Alex Müller

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Received: 14 September 2020; Accepted: 29 September 2020; Published: 15 October 2020



Abstract: This contribution presents a personal account of the influence Karl Alex Müller had on the early stages of my career and the scientific questions about which we exchanged our views over the years. While both our research branched into a variety of topics, the common experimental technique, Electron Paramagnetic Resonance, and the Jahn-Teller effect led to fruitful exchanges of ideas on these matters in semiconducting, metallic and ionic crystals.

Keywords: Electron Paramagnetic Resonance (EPR); ENDOR; Jahn-Teller; color centers; $3d$ impurities; perovskite

Preface: Unexpected, and often rather ordinary encounters determine the path of a young scientist. My encounter with Karl Alex Müller (Alex in the following), winner with G. Bednorz of the 1987 Nobel prize in physics for the discovery of high-temperature superconductivity, was such an encounter when I started my PhD at the University of Geneva. A short time before leaving the Geneva Battelle Institute in 1963, Alex Müller presented a seminar to the group I was a member of. The meeting guided the use of my first experimental tool in research (Electron Paramagnetic Resonance, EPR) and the first steps of my scientific career. Here is a brief recollection of my encounters with Alex over the course of our careers, and some of the scientific questions about which we shared our views.

1. A Group Seminar at the University of Geneva

Alex studied Physics at the Eidgenössischen Technischen Hochschule in Zürich (ETHZ), and completed his doctorate in 1957 in the Institute of Professor Busch with a thesis entitled Paramagnetische Resonanz von Fe^{3+} in SrTiO_3 - Einkristallen. It was published in 1958 [1]. More about it below.

There was one anecdote mentioned to me by Charles Enz that is revealing of Alex's approach to physics. In 1956 Charles Enz completed his doctorate in theoretical physics and became (the last) assistant of Wolfgang Pauli. One of Charles' duties as an assistant consisted in taking care of the library for theoretical physics. Pauli was a frequent user of the library and assumed that Charles was there for his scientific work. The main door to the library was quite noisy. Alex Müller had many questions to ask a theoretician. Having met Charles during his first year as a PhD student at the ETHZ, he looked for ways to obtain some time from him to answer his questions. Alex succeeded in meeting Charles in the library. During one of these meetings they heard the squeaky noisy door. Charles' reaction was immediate: he asked Alex to pack his items and disappear through a side door. Charles knew he had work to do for Wolfgang Pauli. This anecdote reveals that already as a PhD student Alex had the right approach to succeed as a physicist; he did not shy off speaking with colleagues, including theoreticians, to help his understanding of the topic he was working on. An approach we share.

Alex left Zürich in 1958 having been nominated as group leader at the Solid State Physics Division of the Swiss Battelle Centre in Carouge, Geneva. At that institution he created the Electron Paramagnetic Resonance (EPR) group, realized and supervised the construction of an 18 GHz EPR spectrometer to do research on ferro- and antiferroelectric systems. He stayed at Battelle until 1963.

I completed my diploma in experimental physics on the realisation and analysis of an Omegatron mass spectrometer at the University of Bern in 1962. In October of the same year I moved with my wife to Geneva to work as a PhD student in the group of Professor Lacroix at the Physics Institute of the University of Geneva. In Bern I had become much interested in the strongly upcoming area of solid state physics and Geneva offered this field as one of the main streams of its physics curriculum. The topic of my thesis was the study of a color center in natural fluorites with the aid of Paramagnetic Resonance. In 1958 a female student, Anne-Marie Germanier, working in the physics department had observed a peculiar EPR spectrum in rose natural fluorites. My first task was to reproduce this result and to analyze the spectrum. I rapidly realized that the investigation of that specific color center is a challenging undertaking. But I also felt that widening the study, which concentrated mainly on structural aspects of a specific center, could bring new insight on the physics of color centers. This approach would also provide insight into the more general topic of solid state physics for example, by studying the microscopic interactions of electronic and vibrational degrees of freedom in a solid. It would indeed be much more interesting to extend the investigation by selecting individual ions (or molecular entities) that can serve as model systems for studying specific aspects of solid state theory and quantum mechanics. In short, to find such model systems.

My PhD advisor was a theoretician who performed calculations of the level structure of $3d$ ions in crystals. His specialty led him to be a consultant for the physics group at Battelle. In 1963, a few months before Alex left Battelle Roger Lacroix asked him to give an informal seminar to our group, which consisted at that time in Roger and myself.

2. What I Learned at the Seminar

I fondly remember the seminar held in the laboratory space I was occupying. At that time Alex was studying members of the ABO_3 family (Figure 1) containing intentionally introduced $3d$ impurities, using his 18 GHz EPR spectrometer and crystallographic techniques.

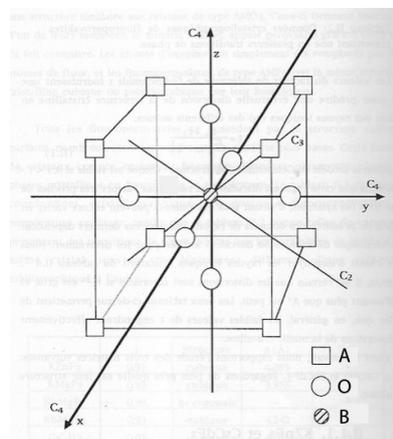


Figure 1. With permission from Reference [2]. Schematic structure of ABO_3 .

He began his talk by presenting EPR results about $Cr^{3+/4+}$, $Mn^{2+/3+}$ and Fe ions introduced as local probes into the crystals [1,3,4]. The g-values, crystal field splittings, hyperfine structure constants (see e.g., Reference [5]) and effects of temperature and external fields on the non-Kramers $3d^2$, $3d^4$, $3d^6$ ground states are signatures of the electronic structure and bonding in the ferroelectric host. Hence, their studies provided a way to monitor structural and electronic properties of the ferroelectric host. Next, Alex analyzed the observed relations between g-values and crystal field effects in these matrices using the theory of Tanabe and Sugano [6]. It occurred to me during Alex's presentation that, indeed, the benefits these "impurities" provided for the investigation of the ferroelectric hosts could, *mutatis mutandi*, also benefit the field of color centers I was interested in. Specific color centers

might be used as “spy ions” or “spy molecules” for the local electronic and vibronic excitations of the host crystal.

There was another insight that would spark my interest for many years to come. In that meeting Alex showed that the Jahn-Teller effect could be responsible for some of his results since degenerate electronic ground states had potentially to be considered as Jahn-Teller active. A concept new to me at the time. When asked about it, he presented the effect and recent developments of the theory of the Jahn-Teller effect. In particular results published by Longuet-Higgins et al. [7] on the static effect and by Frank Ham and Isaac B. Bersuker on the dynamic effect [8–12]. See also Reference [13]. Alex Müller’s talk was a revelation to me as he provided new insight into solid state physics and, at the same time, confirmed and reinforced my point of view adopted at the beginning of my thesis work as mentioned above with respect to the possibility that color centers could provide fundamental insight on the quantum physics of ionic solids.

3. Interaction with Alex Müller during His Activity at IBM Rüschlikon

Visit at IBM in Rüschlikon. In 1975 I had the opportunity to meet Alex in his laboratory. I saw with much interest the magnetic resonance spectrometers he and his group had built. To me it has always been very inspiring to see the solutions other researchers had realized in their experimental setups. In particular, we both had a setup that allowed the application of uniaxial stress and external electric fields. However, the experimental implementations were very different because Alex’s group was studying essentially strongly covalent, semiconducting and metallic samples, while we focused on ionic crystals.

Among the results obtained with his equipment, Alex showed me data from SrTiO₃ doped with Fe³⁺ obtained under uniaxial stress at different temperatures [14]. The electron cloud of the free Fe³⁺ is approximately 12% smaller than the one of Ti³⁺ and has a ⁶S_{5/2} ground state (no orbital degeneracy). It replaces a Ti³⁺ host ion. The EPR results and extracted spin Hamiltonian parameters correspond to a covalent structure with a rather small band gap (~3 eV). Their systems had more explicit many-body effects compared to what we observed in our experiments with the more ionic insulators Na₂S, Li₂S. In the latter, Gd³⁺ (⁸S_{7/2} ground state) introduced in pro mille concentrations served as the spy for ionic diffusion studies. Our experiments were realized beginning 1969 and also included the application of uniaxial stress [15–17].

Most interesting was to learn about his use of the angular overlap model of Newman [18–20]. This model describes the ligand field acting on appropriately chosen paramagnetic spies (e.g., 3d-ions, Rare Earths with electron half-integer spin and orbital-singlet ground state) in a crystal as a linear superposition of the individual spy-ligand interactions. This work uses spies which substitute for a host cation and ideally necessitates precise crystallographical information about the host crystal geometry. The procedure Alex had chosen, as he explained to me, was to use SrTiO₃ and BaTiO₃ crystals. As both compounds show phase transitions and correspondingly different local symmetries of the cation coordination polyheders several local geometries are available and can be examined. The spies he used were Cr³⁺ (goes on both cation sites) or Fe³⁺ (on the Ti site). The EPR experiments they performed provided ligand field terms in the spin Hamiltonian as a function of stress and temperature. By assuming the power-law distance dependency proposed by Newman, experimental parameters for the energy as a function of the individual ligand-spy distance could be obtained. The crystal symmetry properties of the hosts were thereby included. As there are only oxygen anions and the crystals are rather covalent (the local ligand field is predominant) the experiments obtained such dependence of the energy on the cation-oxygen distance for both the A and B cations of the ABO₃ structure. This is, by the way, a beautiful application of EPR. As Alex explained, the application of this method to selected members is an essential step for the understanding of the origin of the phase transitions and electronic level structure of the ABO₃ group (see also Reference [21]).

We applied the Newman model to EPR on the layer perovskites MeFX (Me = Sr, Ba; X = Cl, Br) doped with Gd³⁺ or Eu²⁺. These systems are quite different from those studied by Alex. First, they are

much more ionic (with the exception of BaF₂). Second, two different anionic ligands (e.g., F, Br) instead of one are involved. Hence, two constants had to be determined in the Newman function. Third, the ligand field is made of a superposition of several strong long-range components of partly opposite signs complicating the choice of the power law. Fourth, these hosts are tetragonal (no phase transitions at $p \sim 1$ bar); fortunately, much precise crystallographic information was available. The use of this analysis was motivated by the finding illustrated in Figure 2 (top) that SrFCl:Eu²⁺ showed a large crystal field splitting of almost 6 kG, whereas the Eu²⁺ EPR spectra had practically no splitting in the BaFCl host (bottom of Figure 2), indicating subtle geometric compensations between the individual ligand-spy contributions [22].

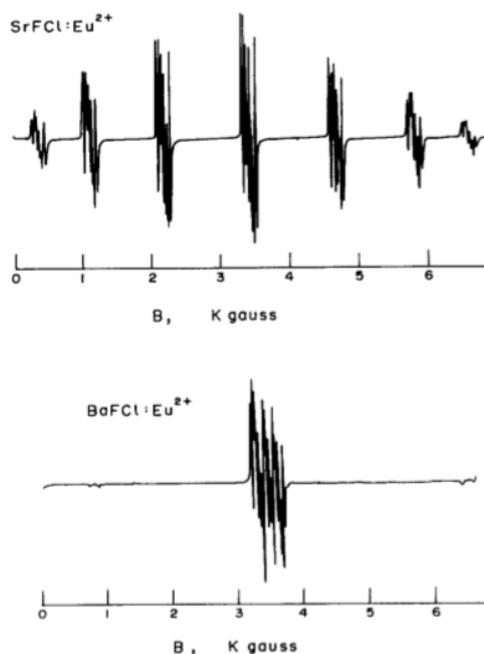


Figure 2. With permission, from Reference [22]. Electron Paramagnetic Resonance (EPR) spectra of Eu²⁺ in SrFCl (**top**) and BaFCl (**bottom**). Measurements were made at 4.2 K with magnetic field parallel to the C₄ axis.

External expert for a PhD on doped CaF₂. During the early research activity on color centers in CaF₂ I had noticed a publication by O'Connor and Chen which presented results related to my research (see References [23,24]). Discussions with Alex Müller at the Swiss Physical Society Meeting in Zürich (1970) and at IBM Rüschlikon strengthened my opinion that this publication deserved further work.

The in-house developed crystal growth setup (see below) allowed to grow a variety of doped CaF₂ crystals and to study the corresponding samples by Paramagnetic Resonance methods at temperatures as low as 1.6 K. A systematic study began in 1983 with one of my physics PhD students, Georges Magne. Alex Müller was one of the external experts for his thesis. The extended investigation was carried out with EPR and Electron Nuclear Double Resonance (ENDOR), both including uniaxial stress or monochromatic light applied to the sample. The dominant center studied consisted of an Y²⁺ substituting for a lattice Ca²⁺ ion. One of the eight F⁻ ions of the surrounding fluorine cube is shifted from its equilibrium position along the [111] direction into a cation free neighboring F⁻ cube, as observed by ENDOR. This results in a trigonal ligand field. Since the ground multiplet of Y²⁺ transforms as Γ_3 in C_{3v} symmetry the trigonal field does not lift this degeneracy of the orbital electronic ground state, resulting in a trigonal E ⊗ e Jahn-Teller effect. The experimental facts that below 20 K the EPR spectrum has symmetry C_s and reacts to uniaxial stress applied along specific directions indicate that a trigonal deformed “Mexican Hat” type potential with three equivalent minima is present. The potential barrier between two adjacent minima is approximately 0.35 eV. The EPR spectrum,

“static” below 20 K, gradually converts into a “dynamical” structure and becomes trigonal around 40 K. A rich superhyperfine structure consisting of 34 lines is observed in the EPR spectrum of the pseudo-static center. The wavefunction of the i th Y 4d electron has admixed contributions of nine F^- , nearest and next-nearest neighbors as explored by ENDOR [25,26].

Several exchanges with Alex Müller regarding the model developed for this system and the experimental results gave way to new insights and orientations to the study. For example, the Frenkel versus Wannier exciton models was debated; the Frenkel exciton was found to be a more adequate description of the system. A still open question about the $\text{CaF}_2:\text{Y}^{2+}$ system is related to the optical absorption spectrum of the Y^{2+} center. There are absorption bands at 630, 490, 330 nm, with oscillator strengths of the order of 0.2–0.4. The short wavelength peaks were identified as arising from $\text{CaF}_2 V_K$, V_F centers but the other band had not clearly been assigned [27]. Tentatively we assigned it to a d - f transition of the 4d electron.

Graduate lectures by K.A. Müller in Geneva. Thanks to the *Convention Inter-Cantonale Romande pour l'Enseignement Du 3ème Cycle en Chimie* I could invite Alex for a series of lectures in Physical Chemistry on “Examples of the Application of Paramagnetic Resonance In Solids” (original title in french). The lectures took place between November 1985 and March 1986 in Geneva, and one at the University of Berne, hosted by Prof. Güdel. The invitation for this series was motivated by the many publications Alex wrote on paramagnetic resonance applied to ferroelectrics, and his focus on Jahn-Teller systems. These very well attended lectures presented the rich work of his group on local and collective (especially ferro-distortive) systems monitored through EPR and where the Jahn-Teller effect plays an essential role. Several invited talks by Alex followed during the next decade, including one to receive the honoris causa doctorate of the University of Geneva.

The Jahn-Teller effect movement. Theoretical and experimental work on the Jahn-Teller effect in systems with a degenerate electronic ground state started in its modern form around 1954. British groups studied model cases for the static lifting of the electronic state degeneracy [7]. Another important progress was made by F.S. Ham and I.B. Bersuker who independently published seminal papers on the dynamic Jahn-Teller effect [8–12]. The vibrant activities around the static and dynamic Jahn-Teller effects motivated the creation of an interdisciplinary symposium, starting in Bad Honneff, Germany, in 1976. The “Jahn-Teller Symposium” gathers theorists and experimentalists, physicists and chemists who present and discuss new developments related to the Jahn-Teller effect. Alex was one of the founding members of the movement. The symposium met on a regular basis in Bad Honneff (Germany), Leoni (Italy), Trento (Italy), Chantilly (France), Oxford (UK), Nijmegen (Netherlands), Liblice (Czech Rep.), Marburg (Germany), Nottingham (UK), Kishinev (Moldova), Ovronnaz (Switzerland), Tartu (Estonia), Berlin (Germany), Erice (Sicily), Boston (USA), Leuven (Belgium), Beijing (China), Trieste (Italy), Heidelberg (Germany), Fribourg (Switzerland), Tsukuba (Japan), Graz (Austria) and Santander (Spain).

The symposium in Ovronnaz (Valais, Switzerland) took place at the end of August 1992 and was organized by the author. Alex agreed to participate. His presentation dealt with the Jahn-Teller polaron idea to explain the electronic level structure of high-temperature superconductors. Figure A1 is the so far unpublished official picture of participants at the Ovronnaz Jahn-Teller symposium, though not all of them are on the picture. Alex is in the first row, sixth from the left, with his wife on his left, and the author and his wife are next on his right. Other persons mentioned in this paper are R. Lacroix at the right end of the first row, F.S. Ham at the right end of the second row and I.B. Bersuker third from the left in the first row. The Appendix A lists the names of participants to the 1992 Jahn-Teller symposium.

4. A Few Common Scientific Interests

Over the years Alex Müller and I worked on quite different aspects of condensed matter physics. Nevertheless, our paths merged time and again on some topics of shared interest. I mention here three that generated fruitful exchanges.

Oxygen centers in the cubic MeF_2 . Around 1965–1966 together with Eric Walker, one of R. Lacroix's diploma student that I was advising, we realized a crystal growth furnace of the Bridgman type which allowed to grow crystals in a controlled atmosphere containing an extremely low fraction of oxygen (in quantities less than a part per million). The resulting monocrystals of 2 to 8 cm³ volume allowed to study oxygen centers, among others, which could be produced under controlled conditions (e.g., by using rare isotopes). Alex showed interest in the setup we had built. Initial work with this furnace and EPR/ENDOR experiments identified the origin of the color of natural rose Fluorites: an ($\text{Y}^{3+}\text{O}_2^{3-}$) molecule [28]. Another system of interest to Alex was the paramagnetic oxygen ion O^- ion substituting for an F^- ion in the CaF_2 lattice. It undergoes a $\text{T}_{2g} \otimes e$ Jahn-Teller effect below ~ 40 K as measured with EPR, and reacts strongly to uniaxial stress applied to the sample crystal [29]. The strongest effects were observed on the O^- ion in SrF_2 [30]. In 1969 we successfully realized exploratory experiments to use this oxygen ion as a cooling engine starting at 1.6 K.

$\text{CaF}_2:\text{La}$ —charge compensation and exciton effects. In 1985, during Alex's lectures at the University of Geneva we had an interesting discussion on “when is the identification of a Jahn-Teller center in a given host established”. The La ion in CaF_2 is doubtlessly a system where this question applies. As-grown crystals from our furnace never showed any Lanthanum EPR signal, indicating the high purity of the samples. But the La^{2+} ion ($5d^1$) appears as a Jahn-Teller system (cubic, $\text{E} \otimes e$), for example, when these crystals are subsequently weakly hydrolyzed and then X-irradiated at 255 K [31]. EPR shows an isotropic spectrum above 16 K and an axial one below about 6K. EPR realized with uniaxial stress applied to the sample demonstrated that the system reorients between the three tetragonal minima of a warped “Mexican Hat” potential. In addition, the EPR spectrum showed the O^- ion mentioned above with all the dynamical features present. Clearly this signaled that the O^- is indeed the Jahn-Teller ion described above. The two centers are mutually independent and the equation of the electron transfer is $\text{O}^{2-} + \text{La}^{3+} \xrightarrow{\text{X-rays}} \text{O}^- + \text{La}^{2+}$. Thus, there is sufficient distance between the two ions that no mutual interaction shows up in the spectra.

Non-hydrolyzed $\text{CaF}_2:\text{La}$. Crystals grown from highest quality powders and excluding any Oxygen, present the most detailed information regarding the Jahn-Teller effect that the La^{2+} ion undergoes. At 4.2 K the EPR spectrum shows 10 lines of 28 Gauss peak-to-peak linewidth (first derivative spectra) due to the Lanthanum ion. Depending on the sample and its treatment a few narrow and weak lines are observed on the low field part of the spectrum when the magnetic field is parallel to a C_4 axis. EPR under uniaxial stress applied to the $\text{CaF}_2:\text{La}^{2+}$ crystal at a temperature of 1.7 K allowed to clarify this situation. At an applied pressure of 5.2×10^8 Pa along a [110] direction and with the applied DC magnetic field \mathbf{B} parallel to the [001] direction, perpendicular to [110], a strong group of 64 narrow lines appeared due to the hyperfine interaction of the electron spin with the La-nucleus and super-hyperfine interaction with a number of F^- nuclei. The g-tensor is axial with $g_{zz} > g_{xx} = g_{yy}$, resulting in only partial overlap of the spectral components. Indeed, the parallel spectrum is on the low magnetic field side (the intense group of 64 lines) and the one perpendicular to \mathbf{B} on the high field side of the spectrum. Both groups overlap, thereby covering 4 of the 8 lines of the perpendicular spectrum. The chosen geometry of the fields applied to the crystal corresponds to the situation where the minimum of the deformed “Mexican hat” potential associated with the parallel component of the EPR spectrum is lowered in energy while the other two minima are pushed up, thereby remaining mutually degenerate. These latter ones are responsible for the perpendicular (8-line) spectral component. This indicates that the parallel spectrum behaves as a Frenkel exciton [32].

Fluoro-perovskites doped with Cu^{2+} . At the XXII Ampère Congress in Zürich my group showed a poster of preliminary results on KZnF_3 doped with Copper. The as-grown crystals presented EPR spectra of Cu^{2+} the symmetry of which depends on growth conditions. The ones shown in Zürich were isotropic at 20 K and “static” at 1.6 K sample temperature. Uniaxial stress was applied to the crystal. Alex passed by and was interested in the Copper data as well as in the details of the crystal preparation. At the time we only had first EPR results. But encouraged by his interest I enlarged the scope of the research to several members of this family (KZnF_3 , CsCdF_3 and RbCdF_3), using Cu^{2+} and

Ag^{2+} as spy ions. The crystals of the $\text{KZnF}_3:\text{Cu}^{2+}$ system remains cubic, the dynamical effects the Cu ion present in the ground state are of the Jahn-Teller type $E \otimes e$ [2,33,34].

5. Concluding Remarks

The recollections in this article span several decades, but only a portion of the scientific questions both Alex Müller and myself addressed in our respective laboratories. They underline the importance of personal scientific exchanges. Our interactions were determinant at the beginning of my career and always constructive thereafter. These fruitful conversations, spread over the years, dealt with details of our common experimental techniques as we applied them to solids with very different physical properties, but also with the physics they revealed and how theoretical works could be applied to describe our experimental findings. I am grateful to Alex for the enriching exchanges on our shared interests.

Funding: This research received no external funding.

Acknowledgments: I thank Andreas Bill (“der junge Bill” as Alex Müller calls him) for feedback on the manuscript.

Conflicts of Interest: The author declares no conflict of interest.

Appendix A. The 1992 Jahn-Teller Symposium in Ovronnaz, Switzerland

Figure A1 is a picture of most participants of the 1992 Jahn-Teller symposium in Ovronnaz, Switzerland, which the author of the paper organized. Following is the list of participants in alphabetic order (not including spouses). The numbers in parenthesis (X, Y) following a name indicate the row and column on the picture for those my recollections allowed to identify. For example, Alex Müller is the sixth person (from the left) in the first row (from the bottom) and thus has the index (1, 6). His wife Inge Müller is the person on his left and has the index (1, 5). The author and his wife are on Alex’s right and have indices (1, 7) and (1, 8), respectively.



Figure A1. Participants of the 1992 Jahn-Teller symposium organized by the author in Ovronnaz, Switzerland. Alex Müller is in the first row, sixth from the left. His wife Inge is on his left. The author and his wife are next on his right. The complete list of participants is in the appendix.

M. Atanasov, C.A. Bates (2,7), I.B. Bersuker (1,3), A. Bill (3,13), H. Bill (1,7), O. Brandt, C.C. Chancey (4,4), F.Th. Chaudron, T.S. Dod, M. Dominoni, J.L. Dunn (2,10), H. Eiermann (3,9), M. Eremin (3,3), A. Furlan, H. Hagemann (3,1), F. S. Ham (2,15), S. Jamila (2,9), Z. Jirak, K.H. Johnson, M. Kaplan (3,4), P.J. Kirk (2,8), R. Lacroix (1,14), W.J.A. Maaskant (4,6), E. Mayerniekova (3,14), R. Meiswinkel, K.A. Müller (1,6), M.C.M. O'Brien (3,5), I. Ohnari (4,5), E.P. Pearl (2,8), H. Reik (3,8), D. Reinen (4,2), U. Schotte, K.D. Schotte (2,3), H.J. Schulz (2,12), E. Sigmund (3,11), Ch. Simmons (1,9), D.R. Taylor (2,5), H. Thomas (4,3), I. Vallin, H. Van d. Waals (4,9), J. Van Tol (4,10), A.M. Vasson (1,2), A. Vasson (1,1), M. Wagner (3,6), R. Willett (4,10), O.A. Yakovleva (1,11).

References

- Müller, K.A. Paramagnetische Resonanz von Fe^{3+} in SrTiO_3 - Einkristallen. *Helv. Phys. Acta* **1958**, *31*, 173.
- Minner, E. Etude Spectroscopique des Ions Jahn-Teller Cuivre et Argent Bivalents dans des Monocristaux de Fluoro-Perovskites de Composition Chimique AMF_3 . Ph.D. Thesis, University of Geneva, Geneva, Switzerland, 1993; Thesis N° 2635.
- Müller, K.A. Electron Paramagnetic Resonance of Manganese IV in SrTiO_3 . *Phys. Rev. Lett.* **1959**, *2*, 341; See also his list of references published on the internet. [[CrossRef](#)]
- Wysling, P.; Müller, K.A.; Hochli, U. Paramagnetic Resonance and Relaxation of Ag^{2+} and Pd_3P in MgO and CaO . *Helv. Phys. Acta* **1965**, *38*, 358.
- Müller, K.A.; Simanek, E.S. *Covalency and Hyperfine Structure Constant A of Iron Group Impurities in Crystals*; RZ 296 (# 11513); IBM Thomas J. Watson Research Center: New York, NY, USA, 1969.
- Tanabe, Y.; Sugano, S. On the Absorption Spectra of Complex Ions. I. *J. Phys. Soc. Jpn.* **1954**, *9*, 753–766. [[CrossRef](#)]
- Longuet-Higgins, H.C.; Öpik, U.; Pryce, M.H.L.; Sack, R.A. Studies of the Jahn-Teller effect. II. The dynamical problem. *Proc. Roy. Soc. Lond.* **1958**, *A244*, 1.
- Ludwig, G.W.; Ham, F.S. Effects of Electric Fields in Electron Spin Resonance. *Bull. Am. Phys. Soc.* **1962**, *7*, 29.
- Ham, F.S. Dynamical Jahn-Teller effect in paramagnetic resonance spectra: orbital reduction factors and partial quenching of spin-orbit interaction. *Phys. Rev. A* **1965**, *138*, 1727. [[CrossRef](#)]
- Bersuker, I.B. Inversion Splitting of Levels in Free Complexes of Transition Metals. *Zh. Eksperim. i Teor. Fiz.* **1962**, *43*, 1315; [English transl.: *Soviet Phys. JETP* **1963**, *16*, 933].
- Bersuker, I.B. Spin-inversion Levels in a Magnetic Field and the EPR Spectrum of Octahedral Cu^{2+} Ion Complexes. **1963**, *44*, 1239; [English transl.: *Soviet Phys. JETP* **1963**, *17*, 836].
- Bersuker, I.B.; Vekhter, G.B. *Fiz. Tverd. Tela* **1963**, *5*, 2432; [English transl.: *Soviet Phys. Solid State* **1964**, *5*, 1772].
- Müller, K.A. *Magnetic Resonance and Relaxation*; Blinc, R., Ed.; North-Holland: Amsterdam, The Netherlands, 1967; Volume 11, p. 192–208.
- Von Waldkirch, T.; Müller, K.A. EPR of Fe^{3+} in SrTiO_3 Under Uniaxial (100) Stress. *Helv. Phys. Acta* **1973**, *46*, 331–339.
- Moret, J.M.; Bill, H. Experimental determination of the spin-stress coefficients of Gd^{3+} in the new host crystal Na. *Phys. Stat. Sol. A* **1977**, *41*, 163–171. [[CrossRef](#)]
- Montaner, A.; Galtier, M.; Benoit, C.; Bill, H. Optical constants of sodium sulphide. *Phys. Stat. Sol. A* **1979**, *52*, 597. [[CrossRef](#)]
- Carron, P.-L. Etude Expérimentale des Effets de Désordre à Hautes Températures dans des Cristaux de Sulfure Alcalins de Structure Anti-Fluorine. Ph.D. Thesis, University of Geneva, Geneva, Switzerland, 1990; Thesis N° 2444.
- Newman, D.J. Theory of lanthanide crystal fields. *Adv. Phys.* **1971**, *20*, 197. [[CrossRef](#)]
- Newman, D.J.; Urban, W. Interpretation of S-state ion EPR spectra. *Adv. Phys.* **1975**, *24*, 793. [[CrossRef](#)]
- Newman, D.J.; Siegel, E. Superposition model analysis of Fe^{3+} and Mn^{2+} spin-Hamiltonian parameters. *J. Phys. C* **1976**, *9*, 4285. [[CrossRef](#)]
- Ritz, D.; Boatner, L.A.; Chatelain, A.; Höchli, U.T.; Müller, K.A. Octahedral Potential in $\text{KTA}_{1-x}\text{NB}_x\text{O}_3$ for an ION 6S5/2- Fe^{3+} . *Helv. Phys. Acta* **1978**, *51*, 430–433.
- Nicollin, D.; Bill, H. Gd^{3+} , Eu^{2+} in SrFCl and BaFCl single crystals: EPR results. *Sol. State Comm.* **1976**, *20*, 135. [[CrossRef](#)]

23. O'Connor, J.R.; Chen, J.H. Color Centers in Alkaline Earth Fluorides. *Phys. Rev.* **1963**, *130*, 1790. [[CrossRef](#)]
24. Alig, R.G. Theory of Photochromic Centers in CaF₂. *Phys. Rev. B* **1971**, *3*, 536. [[CrossRef](#)]
25. Bill, H.; Magne, G.; Balestra, C.; Lovy, D. A trigonally charge-compensated Y²⁺ ion in CaF₂: A Jahn-Teller system. *J. Phys. C* **1986**, *19*, L19. [[CrossRef](#)]
26. Magne, G. Etude Par résonance Magnétique de Centres Photochromiques dans les Fluorures Alcalino-Terreux. Ph.D. Thesis, University of Geneva, Geneva, Switzerland, 1986; Thesis N° 2189.
27. Hayes, W.; Twidell, J.W. The self-trapped hole in CaF₂. *Proc. Phys. Soc.* **1962**, *79*, 1295. [[CrossRef](#)]
28. Bill, H. Investigation of Color Centers in Alkaline Earth Fluorides. Ph.D. Thesis, University of Geneva, Geneva, Switzerland, 1968; Thesis N° 1475.
29. Bill, H.; Silsbee, R.H. Dynamical Jahn-Teller and reorientation effects in the EPR spectrum of CaF₂:O⁻. *Phys. Rev. B* **1974**, *10*, 2697. [[CrossRef](#)]
30. Bill, H. Chapter 13. In *The Dynamical Jahn-Teller Effect In Localized Systems*; Perlin, Y.E., Wagner, M., Eds.; Elsevier: Amsterdam, The Netherlands, 1984; pp. 709–817.
31. Hayes, W.; Twidell, J.W. Paramagnetic resonance of divalent lanthanum in irradiated CaF₂. *Proc. Phys. Soc.* **1963**, *82*, 330. [[CrossRef](#)]
32. Bill, H. University of Geneva, Geneva, Switzerland. Unpublished, 2020.
33. Minner, E.; Bill, H. The Jahn-Teller systems Ag²⁺ and Cu²⁺ in RbCdF₃, an EPR investigation. In Proceedings of the XII International Conference on Defects in Insulating Materials, Schloss Nordkirchen, Germany, 16–22 August 1992; Kanert, O., Spaeth, J.-M., Eds.; Volume 1, p. 571.
34. Minner, E.; Lovy, D.; Bill, H. Electron paramagnetic resonance and relaxation study of copper (II) and silver (II) in CsCdF₃ single crystals. *J. Chem. Phys.* **1993**, *99*, 6378. [[CrossRef](#)]

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