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The defect structure of $CaF_2:U^{3+}$

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Abstract

Neutron diffraction on two single crystals of CaF_2 doped with 6 and 12 mole% UF_3 shows anionic vacancies on the normal F^- ion site and excess anions on an interstitial site F″. The ratio of F″ sites to anionic vacancies and to U^{3+} dopant cation indicates that the cluster is of the 1:0:*n* (*n*=2, 3) type found for homologous $CaF_2:LaF_3$ solid solution. Electron Paramagnetic Resonance measurements on isolated U^{3+} ions (<0.05%) in CaF_2 crystals show they are in a tetragonal site, in which the trivalent U^{3+} ion substitutes for a divalent Ca^{2+} ion with the charge compensation F^- ion along the ⟨100⟩ axis. The local modes of vibration of H^- ions in crystals of $CaF_2:UF_3$ double-doped with H^- ions show clusters for U^{3+} of intermediate dopant concentrations, typically 0.1–10 mole%, and hence have promise to bridge the gap between the concentration ranges for which Electron Paramagnetic Resonance and neutron diffraction are respectively suitable. At very low concentrations, the electron–phonon splitting (0.6 cm^{-1}) of the *xy* vibration of the H^- ion is evident.

Keywords: Clusters; Disordered systems; Neutron diffraction; Electron paramagnetic resonance

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1. Introduction

The alkaline earth fluorides (AF_2=CaF_2, SrF_2 and BaF_2), heavily doped with trivalent ions, have been shown to have two-level-systems, the property that effectively distinguishes a glass from a crystal [1–3]. This system allows ease of study of two-level-systems because of the wide number of variable parameters available: host lattice; dopant concentration; trivalent ion size; trivalent ion mass, and, through uranium, dopant ion valency.

The properties of trivalent ions in AF_2 are mostly well known for sites involving a single trivalent ion. However, two-level-systems are only observed for concentrations for which clusters involving more than one dopant ion exist (i.e. for dopant concentrations greater than 0.1%) [3] and they occur for all higher dopants up to the highest dopant concentration possible in the host (typically 40 mole%).

Structural determinations have been obtained by neutron diffraction for powders involving concentrations typically of 20% and higher [4].

The aim of the current work is to obtain structures for single crystals of $CaF_2:U^{3+}$, particularly at the lowest concentrations applicable to neutron diffraction, and to use electron paramagnetic resonance and spectroscopic methods to bridge the concentration gap between the two techniques (typically 0.1–10% dopant concentration).

2. Structure

The CaF_2 structure can be regarded as a simple cubic array of touching F^- ions, with every second void occupied by a smaller Ca^{2+} ion. The relative ion sizes are such that the Ca^{2+} ions just fit into the void. U^{3+} is similar in ion size to Ca^{2+} so it too fits into a void but needs charge compensation, usually achieved by an extra F^- ion.

Electron paramagnetic resonance studies, using an X-band spectrometer and sample temperatures of 12 K, show that at low concentrations the charge compensating F^- ion is in a next nearest neighbour void to the U^{3+} ion giving tetragonal C_{4v} symmetry to both ions. For $CaF_2:U^{3+}$, $g_{max}=3.5330$ and $g_{min}=1.8789$ [5]. This work also showed that the oxygen scavenger PbF_2 was needed to be added to the melt. Without it, several weak lines were observed in crystals grown without the uranium dopant. These were

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attributed to impurity oxygen ions or, possibly, calcium ion vacancies.

The single ion tetragonal C_{4v} site is also well known from infrared transmission studies of CaF_2 doped with trivalent lanthanide ions and probed with H^- ions [6]. The crystal is heated in contact with molten aluminium in a hydrogen atmosphere so that some hydrogen ions exchange for fluorine ions in the lattice. Hence some of the charge compensating F^- ions are replaced with H^- ions. There are two local mode vibrations of this H^- ion; the broader *z*-mode, in which the H^- ion vibrates along the H^-–Ln^{3+} line, and the doubly degenerate but sharper *xy*-mode, vibrating in the plane perpendicular to the *z*-mode. For the larger lanthanides the *xy*-mode has its degeneracy raised by the electron-phonon interaction [7]. H^- ions have a similar behaviour near U^{3+} in CaF_2 (Fig. 1). The *xy*-mode at 981.5 cm^{-1} has two components separated by 0.6 cm^{-1}. The frequency of the *xy*-mode vibrations of the interstitial H^- ion indicate that U^{3+} is similar in size to a La^{3+} ion.

$Ca_{1-x}Ln_xF_{2+x}$ (Ln=La–Lu, Y) fluorite solid solutions, are well known. X-ray crystallography shows that the structure is overall that of the CaF_2 lattice for trivalent dopant ion concentrations up to 40 mole% [8–11]. Their physical properties have been extensively probed in two-level-system related studies, e.g. low temperature thermal conductivity [12], mm wave transmission [3], relaxation of terahertz phonons [13], Raman Scattering [14], photoconductivity [15], and optical hole burning [16].

X-ray diffraction gives only the averaged structure. Neutron diffraction has shown that the defect structure of these solid solutions are characterized, for high dopant concentration ($x>$mole 5%) by Ca/Ln cationic substitution and by introduction of anionic excess in clusters [4]. These clusters associate anionic vacancies on the normal F ion site, and interstitial anions in two sites: F′ (1/2, x, x; $x\approx0.38$) and F″(x, x, x; $x\approx0.41$). Two kinds of clusters have been described: cuboctahedral clusters for the smaller diameter lanthanides and small 1:0:3 clusters (1 anionic vacancy, 0 F′ and 3 F″ interstitial anions) for the larger diameter trivalent ions (La–Dy). F‴ site (x, x, x; $x\approx0.28$) corresponds to anions relaxed from the normal F site. In the present work, the synthesis of large CaF_2 single crystals containing significant amounts of U^{3+} allowed us to study the defect structure of these phases. Indeed, the U^{3+} cation is rather unstable and few structural and spectroscopic studies involving this cation have been published.

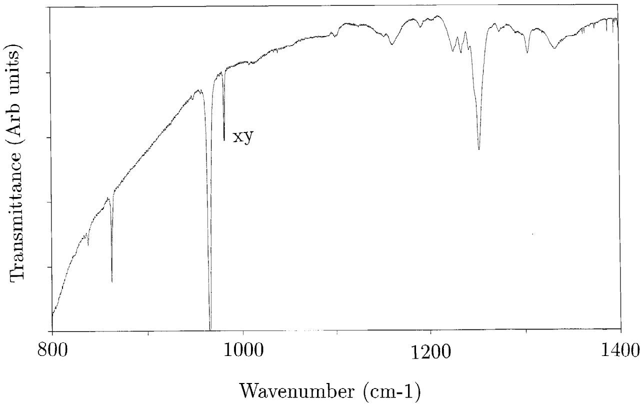

Fig. 1. H^- local mode vibration in calcium fluoride doped with 0.1% trivalent uranium ions. The crystal temperature is 10 K.

3. Preparation and preliminary study

All CaF_2:U^{3+} crystals were grown in graphite crucibles at Canterbury, in an rf heated furnace using the Bridgman–Stockbarger method, either in vacuum or in an inert atmosphere of argon. UF_4 was used as the starting material as UF_3 decomposes below the melting temperature of CaF_2. The graphite crucible reduces U^{4+} to U^{3+}. Radioactive emissions were used to compare the dopant levels of different crystals.

Fig. 1 shows the H^- local mode vibrations for a CaF_2:U^{3+}/H^- crystal with dopant concentration of 0.1% U^{3+}, the minimum concentration for which two-level-systems are readily observed. Apart from the strong line at 965 cm^{-1}, which is due to H^- ions that have exchanged with F^- ions in regular positions in the CaF_2 lattice, and the *xy* doublet at 981 cm^{-1}, the other strong lines are due to clusters of U^{3+} and F^- ions, and, possibly in some cases, oxygen impurities.

4. Defect structure

The defect structure of two single crystals has been investigated after recording the diffracted intensities using the D9 four-circle diffractometer at I.L.L. with a short neutron wavelength (0.98 Å). This kind of apparatus allows us to determine and refine more precisely the position of anionic sites and their occupancy.

The defect structure has been determined with SHELXL-97 [17]. A first refinement incorporating a mixed Ca, U site and a normal F site of the fluorite structure (respectively *4a* and *8c* in the space group *Fm-3m*) has been performed. Then, Fourier-difference calculations (Fig. 2a) allowed to determine the position of excess anions on F″ and F‴ sites. The F″ site seems, on the Fourier-difference map, slightly shifted from the ideal *32f*:x, x, x site (with $x=0.41$) to a x, x, z site with $x=0.41$ and $z=0.38$ but the refinement better converges with F″ in its usual *32f* site and then, this shift has not been considered as significant. After introduction of these atoms in the refinement program, their position, the isotropic thermal vibration factors of all atoms and the occupancy of the three anionic sites have been successively refined.

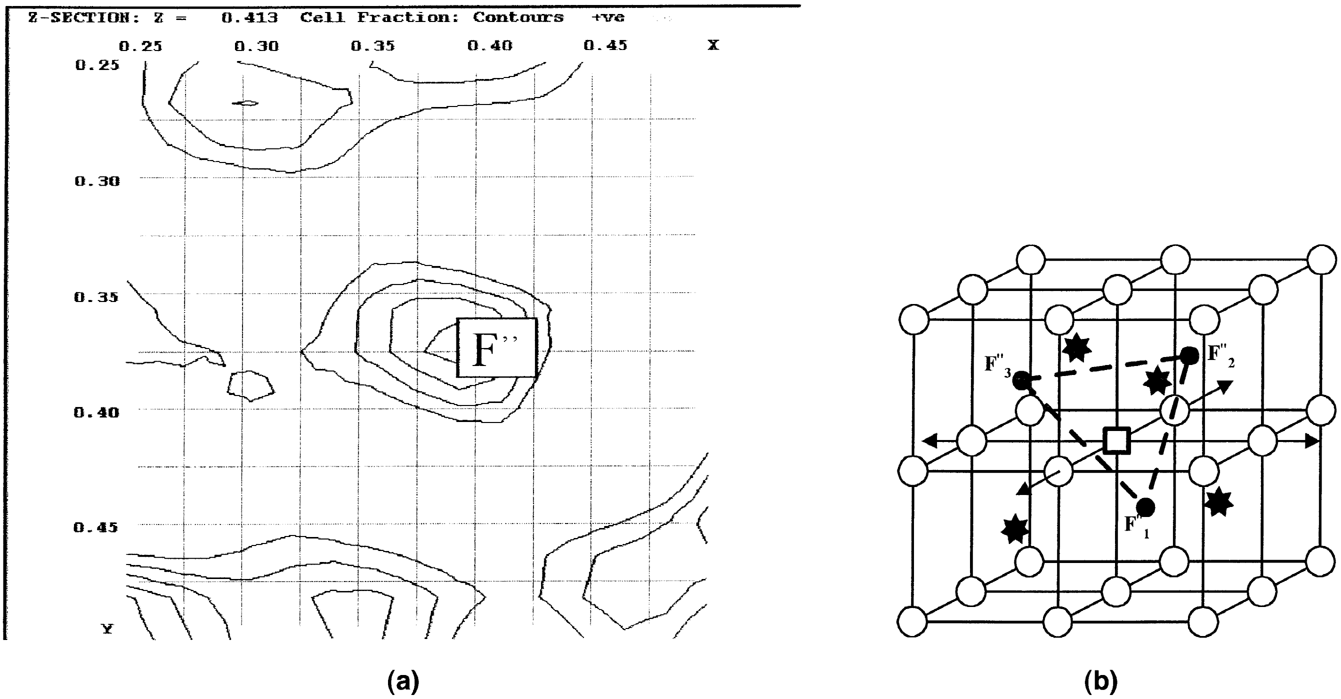

Fig. 2. (a) Fourier-difference map showing the F'''-type interstitial site characteristic of 1:0:3 clusters in CaF_2 doped with 12% U^{3+}; (b) representation of a 1:0:3 cluster.

Finally, since the extinction coefficient was rather high, the three most intense reflections have been removed and a weighting scheme has been introduced. The refinement converged to logical values. At the end, the sum of anion number has been constrained to the experimental value and the same thermal vibration coefficient has been applied to F and F''' sites, very close one to another, in order to decrease correlation problems. The table reports the refined parameters for both phases and a comparison with a single crystal of CaF_2 doped with 10% mole LaF_3, measured with the same apparatus. A great similarity of the atomic positions is clearly evident between U and La-doped phases. The only interstitial site, as shown in Fig. 2a, is of F'' type. It is accompanied by a F''' (relaxed) site. But some differences can be noted between both phases: the ratio $n_{F''}/n_M^{3+}$ (see Table 1), although slightly imprecise because of the limited dopant cation amount, seems higher for U^{3+} dopant than for La^{3+} in the homologous CaF_2: 10% La^{3+} phase which contains 1:0:3 clusters. These clusters (Fig. 2b), associating one anionic vacancy in the F layer and three interstitial F''' anions, have been described for the first time in CaF_2 highly doped with tetravalent cations such as Th^{4+} and U^{4+} and then trivalent cations of large size, e.g. La^{3+}, Nd^{3+} and Dy^{3+}.

It seems logical to consider that doping of calcium fluoride by a cation such as U^{3+}, which is of almost the

Table 1
Refined structural parameters for $Ca_{1-x}U_xF_{2+x}$ and comparison with $Ca_{1-x}La_xF_{2+x}$

Atom	Coord.	6% U^{3+}	12% U^{3+}	10% La^{3+} [9]
Ca, U (La)		0.71(1)	0.91(2)	0.68(2)
F	n	1.70(5)	1.57(9)	1.71(10)
	B	0.81(2)	1.10(8)	0.86(3)
F''	x	0.415(3)	0.414(2)	0.414(6)
	n	0.16(2)	0.30(4)	0.13(4)
	B	2.9(3)	2.7(3)	2.7(8)
F'''	x	0.279(1)	0.284(5)	0.275(6)
	n	0.20(4)	0.25(9)	0.23(9)
	B	0.81(2)	1.10(8)	0.86(3)
	R_1	0.013	0.032	0.028
	$n(v_F)$	0.10	0.18	0.06
	$n(v_F)/n(M^{3+})$	1.7	1.5	0.6
	$n(F'')/n(v_F)$	1.6	1.7	2.2
	$n(F'')/n(M^{3+})$	2.7	2.5	1.3
	a_F (Å)	5.4983(2)	5.5307(2)	5.520(3)

same size as La^{3+}, induces a similar clustering. However, the proportion of interstitial anions and anionic vacancies is higher for U^{3+} and more similar to the values obtained when the dopant cation is tetravalent (U^{4+}, Th^{4+}). Indeed, the stability of the cluster implies its local electrical neutrality which is obtained by a preferential localisation of one M^{4+} or two M^{3+} dopant cations as the close neighbours of the excess F″ anions inside each cluster.

Such a difference in the cationic short range order inside 1:0:3 clusters between U^{3+} and La^{3+} dopant cations and on the contrary the similarity with U^{4+} dopant cation could be understood in imagining that the crystal growth and further equilibrium of the solid solution occurs in two steps:

- a solid state reaction between CaF_2 and UF_4 giving a solid solution $Ca_{1-x}U_x^{4+}F_{2+2x}$ with isolated U^{4+} cations (one for each cluster) and electrical neutrality,
- an in situ reduction process giving U^{3+}, under the reducing influence of the graphite crucible, but without further cationic diffusion, then preserving the isolated U^{3+} cations.

Moreover, the $n_{F''}/n_{VF}$ ratio is close to two, value characteristic of a less dense 1:0:2 cluster (instead of three for a 1:0:3 cluster), which also suggests that the in situ reduction should favour the formation of neutral 1:0:2 clusters about isolated U^{3+} cations.

5. Conclusions

Neutron diffraction of single crystals of CaF_2:U^{3+} shows, for uranium concentrations of 6 and 12 mole% of U^{3+}, anionic vacancies on the normal F^- ion site for the CaF_2 lattice and excess charge compensating anions on an interstitial site (F′″). The ratio of these sites indicate that the cluster is of the 1:0:n type found for homologous CaF_2:Ln^{3+} solid solutions, with $n=2$ or 3.

Another technique, such as the local mode vibrations of H^- ions substituted for F^- ions, both in regular lattice and charge compensating positions, is needed to bridge the gap between low concentrations, where Electron Paramagnetic Resonance is useful, and high concentrations, where neutron diffraction delivers the structures. This gap is the concentration range of interest for the onset of two-level-systems.

References

[1] D.G. Cahill, R.O. Pohl, Phys. Rev. B 39 (1989) 10477.
[2] S.K. Kazanskii, JETP Lett. 41 (1985) 224.
[3] S.A. FitzGerald, J.A. Campbell, A.J. Sievers, Phys. Rev. Lett. 73 (1994) 3105.
[4] J.P. Laval, A. Mikou, B. Frit, G. Roult, Solid State Ionics 28–30 (1988) 1300.
[5] M. Foster, MSc Thesis, University of Canterbury, 1993.
[6] G.D. Jones, S. Peled, S. Rosenwaks, S. Yatsiv, Phys. Rev. 183 (1969) 353.
[7] I.T. Jacobs, G.D. Jones, K. Zdansky, R.A. Satten, Phys. Rev. 3 (1971) 2888.
[8] J.P. Laval, A. Abaouz, B. Frit, A. Le Bail, J. Solid State Chem. 85 (1990) 133.
[9] J.P. Laval, A. Abaouz, B. Frit, J. Solid State Chem. 81 (1989) 271.
[10] R. Roth, T. Negas, L. Cook (Eds.), Phase Diagrams for Ceramists, Vol. 5, The American Ceramic Society, 1983.
[11] N.B. Grigoreva, L.P. Otroschchenko, B.A. Maksimov, I.A. Verin, B.P. Sobolev, V.I. Simonov, Crystallogr. Reports 41 (1996) 4.
[12] K. Topp, E. Thompson, R.O. Pohl, Phys. Rev. B 60 (1999) 898.
[13] P. Fischer, K. Renk, J.A. Campbell, U. Happek, J. Lumin. 58 (1994) 14.
[14] J. Tu, J.A. Campbell, A.J. Sievers, J. Non-Cryst. Solids 203 (1996) 153.
[15] M. Raukus, J. Choi, J.A. Campbell, U. Happek, J. Lumin. 72 (1997) 250.
[16] K.W. Jang, K.S. Hong, T.T. Basiev, R.S. Meltzer, J. Lumin. 66–67 (1995) 8.
[17] G.M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, Gottingen University, 1997.