Positron annihilation in UF_4-doped BaF_2

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Abstract. UF_4-doped BaF_2 has been investigated by positron annihilation spectroscopy. The doping causes the angular correlation spectra to broaden and the mean positron lifetime to decrease. It is proposed that this atypical behaviour for positrons in defected materials is explained by positron trapping and annihilation from defect clusters with excess F^- ions.

1. Introduction

Positron annihilation spectroscopy has been utilised for extensive studies of materials— and especially of defects in metals (Brandt and Dupasquier 1983). Studies on ionic crystals have primarily been performed on nominally pure and perfect crystals. The positron can reside in several states in such crystals and the experimental positron lifetime spectra are complex and consist typically of at least three decay components (Linderoth *et al* 1986).

The angular correlation curves for the two annihilation γ-rays, measured on alkali halide crystals, are considerably narrower than expected from theoretical calculations (Nieminen 1975). The complexity of the positron lifetime spectra and the narrowness of the angular correlation curves have recently been explained as corresponding to positron trapping at defects created in the last few hundred ångstrom's of the slowing-down spur of the positron itself (Linderoth *et al* 1986, Shishkin *et al* 1988). The non-trapped positron is probably in a polaron state and the annihilation characteristics in this state are, primarily, determined by the negative halide ions (Nieminen 1975).

Angular correlation curves for aqueous solutions of alkali halides (Mogensen 1979) and polyacetylene doped with the same halide ions (Cartier *et al* 1985) have shown that the positron can be trapped and annihilate at Br^-, Cl^- and I^- ions, whereas no binding of the positron to the F^- ion was observed. We present angular correlation and positron lifetime results for BaF_2 doped with UF_4. The results suggest that the positron annihilates from states localised near interstitial fluoride ions.

2. Experimental details

The $Ba_{1-x}U_xF_{2+2x}$ ($x = 0.0077, 0.158, 0.33, 0.7, 2$ and 8%) samples were prepared as described by Andersen *et al* (1983). Inelastic neutron scattering results suggest that so-

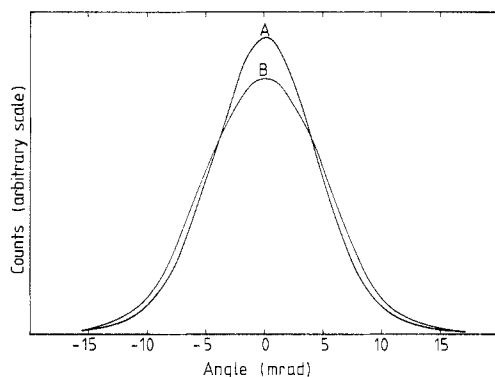† Permanent address: Moscow Physical Engineering Institute, Moscow, USSR.

Figure 1. The normalised angular correlation curves for $Ba_{1-x}U_xF_{2+2x}$ with x equal to (A) 0 and (B) 0.7%.

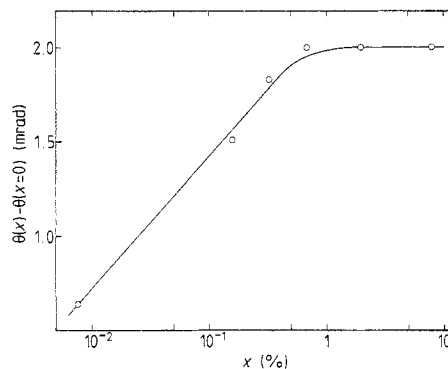**Figure 2.** The change in the full width at half maximum, θ, of the angular correlation curve for $Ba_{1-x}U_xF_{2+2x}$ as a function of x.

called (212) clusters are formed by the doping (Andersen *et al* 1983), where the U^{4+} ion, substituting for a Ba^{2+} ion, is surrounded by four F^- ions—two relaxed substitutional ions and two interstitial F^- ions.

The angular correlation spectra have been acquired with a conventional long-slit machine (MacKenzie 1983) with an optical resolution of 1 mrad. The positron lifetime measurements were performed with a conventional fast–slow timing spectrometer (MacKenzie 1983) with a time resolution of about 275 ps. All the measurements were made at 295 K. The spectra were analysed with the aid of the POSITRONFIT and PARAFIT programs (Kirkegaard *et al* 1981).

3. Results

The full width at half maximum, θ, of the angular correlation curve for the nominally pure BaF_2 was found to be 11.07 mrad, which is in accord with the value of about 11.7 mrad found for NaF (Linderoth *et al* 1986). In the case of alkali halides the angular correlation spectra for chloride salts were significantly narrower (9.2–9.4 mrad), in accord with theory (Farazdel and Cade 1977).

For pure BaF_2 the positron time spectrum was decomposed into three exponentials with corresponding lifetimes of 120, 300 and 600 ps and intensities of 20, 70 and 10%, respectively, yielding a mean positron lifetime of 300 ps. When a three-state trapping model is applied the positron polaron lifetime is deduced to be about 235 ps (Shishkin *et al* 1988).

Doping of BaF_2 with UF_4 was found to decrease the mean positron lifetime. For x larger than 0.158% the mean positron lifetime remained constant, within statistical uncertainties, and only one lifetime component, with a value of about 240 ps, could be resolved.

The angular correlation curve was found to broaden considerably when BaF_2 was doped with UF_4. In figure 1 the angular correlation curves for $x = 0\%$ and $x = 0.7\%$ are shown. θ has saturated at a value of 13.10 mrad for $x = 0.7\%$. The change in θ as a function of x is shown in figure 2.

4. Discussion

Typically, when defects are introduced into materials it is reflected in the positron annihilation characteristics as a narrowing of the angular correlation curve, an increase of the mean positron lifetime and an increased complexity of the positron spectrum; e.g., several decay components appear (Brandt and Dupasquier 1983). In the present case the opposite effect is seen: the angular correlation curve broadens, the mean positron lifetime decreases and the positron lifetime spectrum changes from a spectrum with at least three decay components to one with a single decay component. The doping causes the positron to annihilate from a single state with a positron lifetime close to that proposed for the polaron state in nominally perfect BaF_2 (Shishkin *et al* 1988) where the annihilation characteristics are governed primarily by the F^- ions. This, in turn suggests that the F^- ions, surrounding the U^{4+} ions for charge conservation, act as effective positron traps. This seems to be the first time that positron trapping at F^- ions has been observed. When about 0.5% of the Ba^{2+} ions have been substituted by U^{4+} all positrons are annihilated from the state, which supposedly is around (212) clusters. Then the distance between the defect clusters is of the order of 100 Å.

5. Conclusions

BaF_2 doped with UF_4 has been studied by positron annihilation spectroscopy. The doping introduces defects that are believed to form so-called (212) clusters. The positron annihilation results show an atypical behaviour: the angular correlation curve broadens and the mean positron lifetime decreases when the defects are introduced. The results can be understood as indicating positron trapping and annihilation at F^- ions in the defect clusters. When more than 0.5% of the Ba^{2+} ions are substituted for with U^{4+} ions the doping effect saturates and the corresponding annihilation characteristics may be close to those for the $[F^-, e^+]$ complex. The results suggest that $\theta \simeq 13$–14 mrad and $\tau \simeq 240$ ps for the $[F^-, e^+]$ complex.

Acknowledgments

References

Andersen N H, Clausen K and Kjems J K 1983 *Solid State Ion.* **9 + 10** 543
Brandt W and Dupasquier A (ed.) 1983 *Positron Solid State Physics* (Amsterdam: North-Holland)
Cartier E, Heinrich F, Kiess H, Wieners G and Monkenbusch M 1985 *Positron Annihilation* ed. P C Jain, R M Singru and K P Gopinathan (Singapore: World Scientific) p 218
Farazdel A and Cade P E 1977 *J. Chem. Phys.* **66** 2612
Kirkegaard P, Eldrup M, Mogensen O E and Pedersen N J 1981 *Comput. Phys. Commun.* **23** 307
Linderoth S, Rajainmäki H, Hansen H E and Nieminen R M 1986 *J. Phys. Soc. Japan* **55** 4504
MacKenzie I K 1983 *Positron Solid State Physics* ed. W Brandt and A Dupasquier (Amsterdam: North-Holland) p 196
Mogensen O E 1979 *Chem. Phys.* **37** 139
Nieminen R M 1975 *J. Phys. C: Solid State Phys.* **8** 2077
Shishkin A V, Linderoth S and Svirida S V 1988 *Phys. Status Solidi* b **149** 785