Temperature Dependence of O_3^- Electron Paramagnetic Resonance Signals in KCl

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An ozonide molecular ion O_3^- has been detected by EPR spectroscopy in KCl single crystals doped with 2% KNO_3 in the melt and X-irradiated at room temperature. The temperature dependence of the O_3^- EPR signals was investigated from 10–60 K and a gradual transition from monoclinic to orthorhombic g-tensor symmetry was found. An unexpectedly strong variation of two principal g values, one corresponding to the direction perpendicular to the molecular plane, the other with the axis connecting the two outer oxygens, was observed. These results are discussed in relation to the possible allocation of the O_3^- to a mono- or a tri-vacancy site. The latter model has been well established by other authors for S_3^- and Se_3^- defects in several alkali-metal halides. Other defects with an electronic structure comparable with that of O_3^-, for instance SO_2^- and SeO_2^-, are believed to replace only one halide ion.

In two recent papers the presence of the ozonide ion, O_3^-, was demonstrated in alkali-metal halide single crystals, X-irradiated at room temperature (RT).[1,2] In other lattices the O_3^- ion has been known for a long time (see *e.g.* ref. 3 and 4). Until very recently we could only detect O_3^- in KCl and KBr doped with KNO_2 and KNO_3 respectively. It was rather peculiar to find that in KCl two g-tensor principal axes of the O_3^- ion were strongly tilted away from ⟨110⟩ and ⟨001⟩ directions in a {1$\bar{1}$0} plane, whereas in KBr the O_3^- ion exhibits orthorhombic symmetry (g_x, g_y, g_z axes parallel to ⟨1$\bar{1}$0⟩, ⟨110⟩, ⟨001⟩). The assignment of the observed EPR signals to O_3^- hardly posed any problems because the latter ion has very characteristic principal g values which depend very little on the host lattice.[1–4] However, a precise model for the O_3^- ion and its nearest environment could not be established so far, as the question arose whether the O_3^- ion occupies only one or three lattice sites. From the early EPR work of Schneider *et al.*[5] and the electron nuclear double resonance (ENDOR) study by Suwalski and Seidel,[6] it was shown that the tri-atomic chalcogenide ions, S_3^- and Se_3^- ions, occupy three lattice sites replacing one alkali and two halide ions. The same authors[5] proposed a single-vacancy model for SO_2^- and SeO_2^- which also have an electronic structure comparable with that of O_3^-. Indeed there is a clear qualitative difference between the g-tensor axes of mono- and tri-vacancy defects: the g value most close to $g_e = 2.0023$ is measured along the ⟨110⟩ and ⟨001⟩ directions, respectively. In this context it may be mentioned that recently a mono-vacancy PO_2^{2-} defect was identified in KCl.[7]

In view of these results it seems, *a priori*, most plausible to assume a single-vacancy model for the even smaller O_3^- ion. The KBr–O_3^- g-tensor is in perfect agreement with such a model. For KCl–O_3^- however the situation is less clear: the g-tensor we found formerly has monoclinic-I symmetry and in addition indications were found that in the KCl–KNO_2 crystals used, other O_3^- resonances were present.[1] For the present study we were fortunate to investigate the same O_3^- signal in KCl–KNO_3 as a function of temperature without too much interference from EPR signals originating from other paramagnetic species.

Materials and Methods

Sample Preparation

Single crystals were grown by the Kyropoulos method.[8] The KCl powder (Merck suprapur) was mixed with 2% KNO_3 (Merck suprapur). The crystals were X-irradiated at RT for typically 10 min with a tungsten anticathode Philips X-ray tube. This corresponds, approximately, to a dose of 13.2 kGy.

EPR

The EPR spectra were recorded using consecutively a Varian E-line and a Bruker ESP300 Spectrometer, both with 200 mW maximum microwave power available. In our particular situation the Varian and Bruker X-band spectrometers operate at *ca.* 9.18 and 9.47 GHz, respectively. Measurements at these two slightly different X-band frequencies are often sufficient to check the frequency dependence of some resonance positions and to detect in this way *e.g.* ^{14}N hyperfine lines. All spectra were stored in digital form with a resolution of 10^{-5} T or better. All spectra were renormalized to the same frequency *viz.* 9.47 GHz. Temperatures down to 2 K can be realized using an Oxford Instruments ESR 10 flow cryostat, available on both spectrometers.

Results

Although KNO_3 was used instead of KNO_2 for the doping of the KCl single crystals,[1] qualitatively comparable EPR spectra were found with resonances mainly from O_2^-, NO_2 and O_3^- radicals. Whereas in the KCl–KNO_2 crystals only a narrow experimental temperature (±4 K) and microwave power (0.01 mW) window allowed the detection of O_3^-, experimental conditions were more favourable in the KCl–KNO_3 case. These radicals are stable up to RT. In the temperature range 6–10 K the optimum detection power is around 0.02 mW. Fig. 1 shows the angular variation at 10 K and 0.02 mW in a {001} plane. Within experimental error the same g-tensor as reported earlier was found, with two principal axes perpendicular to ⟨1$\bar{1}$0⟩ and the same tilting angle α (Table 1). This already suggests that the tilting is not due to some accidental impurity.

Raising the temperature to *ca.* 60 K and then recording the EPR spectra at 0.02 mW microwave power, yields a g-tensor with orthorhombic symmetry (Fig. 2). At 60 K the orientation of the principal axes and the principal values of the g-tensor are in qualitative agreement with the KBr–O_3^- case, which was detected under comparable conditions of temperature and microwave power.[2] However, the g-tensor principal values, especially g_x and g_y differ considerably from the KBr–O_3^- values and also from the KCl–O_3^- values at 10 K (2.0055, 2.0163 at 60 K compared with *ca.* 2.003, 2.018 for

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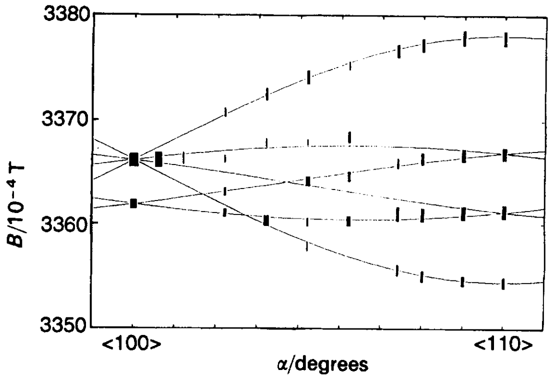


Fig. 1 Angular variation of the O_3^- resonances in a {001} plane at 10 K and 0.02 mW. The rectangles denote the experimental points (the height and width of the rectangles are proportional to the line-width and signal height, respectively). The full curves are calculated with the g-tensor of Table 1 (ν = 9.47 GHz).

KCl at 10 K and KBr). The average g value $\langle g \rangle$, however, coincides within experimental error at 10 K and 60 K (see Table 2). This prompted us to investigate the temperature dependence of the EPR spectrum of KCl–O_3^-. We measured the $\langle 100 \rangle$ and $\langle 110 \rangle$ spectra at 10, 15, 20, 30, 35, 40, 50 and 60 K (Fig. 3). Clearly a gradual transition from monoclinic-I

Table 1 g-tensor of the KCl–O_3^- signal at 10 K and 0.02 mW, compared with earlier work

	g_x $\langle 1\bar{1}0 \rangle$	g_y $(\langle 110 \rangle + \alpha)$	g_z $(\langle 001 \rangle + \alpha)$	$\langle g \rangle$	α/degrees
KCl–KNO_2 [a]	2.0032	2.0182	2.0118	2.0111	25
KCl–KNO_3 [b]	2.0030	2.0183	2.0117	2.0110	24
KBr–KNO_3 [c]	2.0027	2.0180	2.0113	2.0107	0

[a] Ref. 1. [b] This paper. [c] Ref. 2.

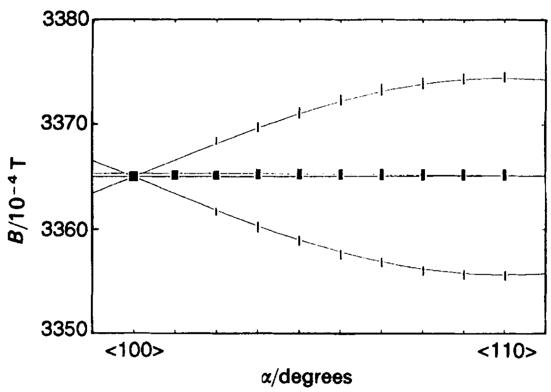


Fig. 2 Same as Fig. 1 at 60 K and 0.02 mW. The full curves are calculated with the g-tensor of Table 2 (60 K)

Table 2 Temperature dependence of g-tensor parameters in the temperature region 10–60 K

T/K	g_x	g_y	g_z	α/degrees	$\langle g \rangle$
10	2.0030	2.0183	2.0117	24	2.0110
20	2.0037	2.0181	2.0109	24	2.0109
30	2.0046	2.0173	2.0107	15	2.0109
35	2.0048	2.0171	2.0107	12	2.0109
40	2.0050	2.0169	2.0108	10	2.0109
50	2.0052	2.0165	2.0105	1	2.0107
60	2.0055	2.0163	2.0107	0	2.0108

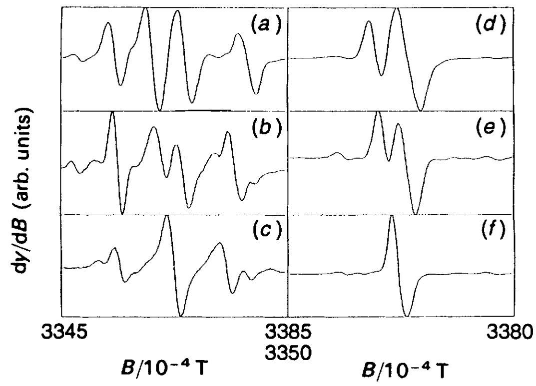


Fig. 3 O_3^- spectra measured along $\langle 110 \rangle$ [(*a*) 10, (*b*) 30 and (*c*) 50 K] and $\langle 100 \rangle$ [(*d*) 10, (*e*) 30 and (*f*) 50 K]

to orthorhombic-I symmetry occurs in this temperature range.

The EPR line positions measured with $\boldsymbol{B}$ along the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions suffice to calculate g_x, g_y, g_z and α. In Table 2 and Fig. 4 these values are presented as a function of temperature. A full angular variation was also carried out at 30 K confirming the results in the principal g-tensor directions.

Above 60 K the O_3^- signals become too weak, compared with some spectra originating from nitrogen containing defects, to allow unambiguous g-tensor determinations. It cannot be excluded however that some kind of O_3^- resonances remain up to even 200 K.

Discussion

In spite of the relatively drastic variation of the g_x and g_y values with temperature, there can be hardly any doubt about the identity of the paramagnetic defect responsible for the observed EPR signals, *i.e.* the ozonide ion (O_3^-). The theory of the free molecular ion with C_{2v} symmetry is fairly well established: the smallest g-value (g_x) is found with the magnetic field perpendicular to the molecular plane, the largest g-value (g_y) is found along the axis connecting the outer equivalent oxygens (O_I and O_{II}) while the intermediate value corresponds with the C_{2v} symmetry axis. This apex angle is generally accepted to take values between 110 and 120°. In an LCAO-MO approximation the unpaired electron resides in an antibonding molecular orbital with B_1 symmetry, composed of p_x, p_{xI} and p_{xII} atomic orbitals. As a consequence one immediately finds $g_x \approx g_e = 2.0023$. Within the same scheme the g_y and g_z values can be predicted qualitatively even without any sophisticated calculation.[3,4]

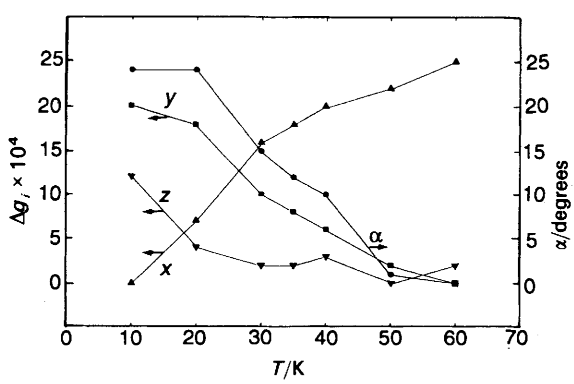


Fig. 4 Temperature dependence of g_x, g_y, g_z and α. The Δg_i ($i = x, y, z$) values are referred to the minimum values encountered in the temperature range 10–60 K.

However it is clear at once that some of the observed g-tensor variations cannot be adequately described within such an approximation.

At this point it is useful to establish whether the spectra observed in KCl at different temperatures are due to essentially the same O_3^- species or not. In view of the continuous variation of the spectrum as a function of temperature and considering that we never observed two O_3^- spectra simultaneously, it seems probable that the EPR spectra originate from the same radical, the latter exhibiting a peculiar temperature dependence. Finally the value of $\langle g \rangle$, which is temperature independent within experimental error, also agrees with this assignment.

For KBr[2] a fairly consistent model could be proposed wherein the O_3^- ion replaces one halide ion. The molecular plane coincides with a $\{1\bar{1}0\}$ plane yielding the smallest g value in a $\langle 1\bar{1}0 \rangle$ direction. As already mentioned in the introduction section, this is at variance with the tri-vacancy model for S_3^- and Se_3^- (smallest principal g value along $\langle 001 \rangle$) but in agreement with the model for smaller molecules like SO_2^- and PO_2.[2–5,7] For the KCl–O_3^- ion under discussion also a model with the O_3^- ion in a $\{1\bar{1}0\}$ plane should be considered. However, several questions immediately arise. Whether the molecular ion undergoes some kind of thermally stimulated motion in a $\{1\bar{1}0\}$ plane or not, it is not, *a priori*, clear why the molecule is tilted in the latter plane at the lower temperatures. Neither is it evident how the g_x value may differ so much from g_e, especially at 60 K.

One should also consider the apparent contradiction with KBr–O_3^- in the sense that at 10 K the KCl–O_3^- principal g values are in nearly perfect agreement with KBr–O_3^-, with the wrong symmetry, however. When the temperature is raised the symmetries become equal with relatively strong g value differences.

Evaluating possible models, the following theoretical and experimental data may be useful:

(1) CNDO/II and INDO calculations show an increasing trend for g_y and g_z when the intramolecular distances increase.

(2) For S_3^- and Se_3^- in alkali-metal halides, g_y and g_z increase and g_x decreases going from smaller halide ions to larger ones.[5]

As at 60 K both KCl–O_3^- and KBr–O_3^- have orthorhombic symmetry and zero tilting angle, we assume the same model in both cases. Although in this model O_3^- occupies a similar site in KBr and KCl, it seems that in the latter case, because of the smaller g_y and g_z values and larger g_x (see Tables 1 and 2), the ozonide has less space.

On the other hand, at 10 K, the O_3^- seems to have sufficient room, as the principal g values are nearly identical in both lattices, but in KCl satisfactory accommodation could be found only by additional tilting.

As far as the large tilting angle is concerned one might suspect the presence of an accidential impurity in the $\{1\bar{1}0\}$ molecular plane (*e.g.* a nitrogen-related defect). In view of the fact that the tilting angle seems to be independent of the doping procedure (KNO_2 or KNO_3) a more fundamental reason might be required. We believe that it is important to consider the latter ion as a three-dimensional entity. Indeed the unpaired electron resides mainly in an antibonding MO pointing along the x direction, perpendicular to the molecular plane ($yz = \{1\bar{1}0\}$ plane):

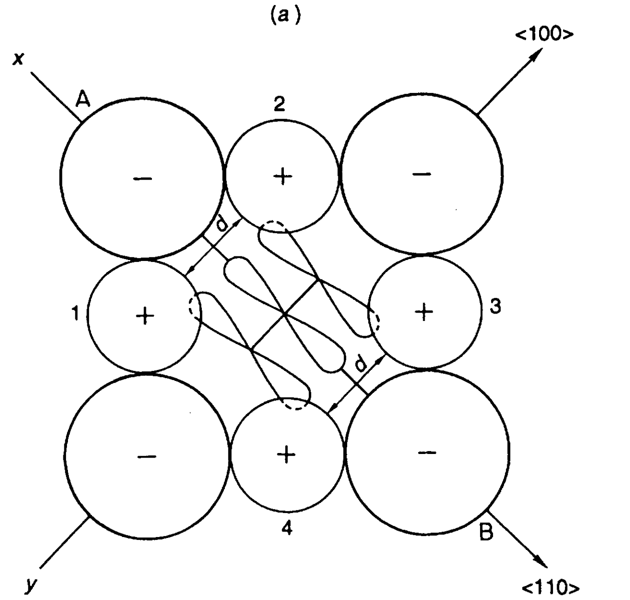
$$|b_1\rangle = -c_1 p_x + c_2 \frac{p_{xI} + p_{xII}}{\sqrt{2}}$$

In such a view it is logical to consider also the four closest neighbour K^+ ions in the $\{001\}$ plane [see Fig. 5(*a*)]. Even the two Cl^--ions in the x direction [labelled A and B in Fig. 5(*a*)], though further away, are possibly important in establishing a model for O_3^-. In Fig. 5 the ionic radii of K^+ and Cl^- ions were drawn to scale, in order to account for the electron clouds around the nuclei.

Considering then both Fig. 5(*a*) and (*b*), we find that the closest $K^+(1)$–$K^+(2)$ distance (labelled d) in a hard-sphere model [see Fig. 5(*a*)], which is ± 0.20 nm for KBr and ± 0.18 nm for KCl, may be relevant in proposing an O_3^- model. Indeed the O_I–O_{II} distance in O_3^- [taken between the centres of the nuclei and labelled D in Fig. 5(*b*)] is typically around 0.20 nm. Furthermore it may be expected that the p_x lobes of the central oxygen try to avoid the A and B Cl^- ions.

For the lowest temperature, this leads us to a model wherein the ozonide ion is off-centre, the central oxygen

(*a*)



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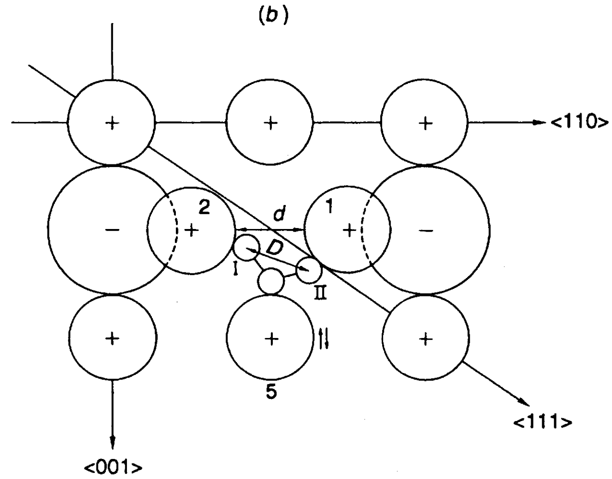

Fig. 5 (*a*) Untilted model for the O_3^- ion in KCl in a $\{001\}$ plane. It is demonstrated that the A and B Cl^- ions and the 1, 2, 3, 4 K^+ ions should be considered in the O_3^- configuration. The ozonide ion should be off-centre along $\langle 001 \rangle$. In this way the p_x lobe of the central oxygen avoids the A and B Cl^- ions while the outer oxygens are out of the region with minimum $K^+(1)$–$K^+(2)$ and $K^+(3)$–$K^+(4)$ distance d (0.20 nm for KBr, 0.18 nm for KCl). (*b*) Tilted model for the O_3^- ion in KCl in a $\{1\bar{1}0\}$ plane. Even with the displacement along $\langle 001 \rangle$ as discussed in (*a*) the KCl–O_3^- has to tilt to find sufficient accommodation.

taking the lowest (or equivalently the highest) position along ⟨001⟩ in Fig. 5(*b*). In this way the p lobe of the central oxygen avoids the two closest Cl^- ions and the outer oxygens are out of the region with minimum $K^+(1)$–$K^+(2)$ distance.

Assuming for O_3^- also some kind of hard-sphere model, it is found that for KBr the O_3^- ion fits in perfectly (Fig. 6) but for KCl the O_3^- ion can only be accommodated by letting it tilt as indicated in Fig. 5(*b*). The value of the tilting angle can be checked to correspond fairly well with that found experimentally. It is important to note that in this model no distance changes within the O_3^- ion have to be assumed, what may explain the nearly identical principal g values for KBr–O_3^- and KCl–O_3^- at 10 K.

Having established a possible model at 10 K, the problem of the behaviour at higher temperature remains. A dynamical model wherein the molecular ion might be thought to occupy two (or four) equivalent positions in a $\{1\bar{1}0\}$ plane between which it jumps at an increasing rate with increasing temperature, seems improbable: the g_y and g_z values are expected to average while the g_x value should remain unaffected, at variance with the experiment. Furthermore, the linewidths in the spectra are expected to change considerably. In Fig. 3 no such behaviour can be found. Finally, with such a model the gradual decrease of the tilting angle with temperature also seems difficult to explain.

A static model with only distances increasing with temperature and so diminishing the possible interactions of O_3^- with the neighbouring ions, seems not very probable in view of the weak temperature dependence of the lattice constant (a few thousandths of an nm in that temperature range). Maybe this could explain the gradually diminishing tilting angle but not the smaller accommodation compared with KBr and the situation at 10 K as discussed above. A possible explanation may be that the K^+ ion [labelled 5 in Fig. 5(*b*)] closest to the central oxygen vibrates at higher temperatures with gradually increasing amplitude in the ⟨001⟩ direction, thereby pushing the O_3^- molecular ion towards a more central position along ⟨001⟩. In this way the ozonide ion would, part of the time, become squeezed between the latter K^+ ion and four {001} K^+ ions, reducing its intramolecular distances. As discussed above, this would result in a decrease of g_y and g_z. In the second half of the vibration period the O_3^- molecular ion will probably return merely to the free ion positions. On the average the O_3^- ion will thus be compressed. The gradual decrease of the tilting angle with temperature would be best explained if the four {001} K^+ ions [Fig. 5(*b*)] move outwards while the other K^+ ion moves inwards.

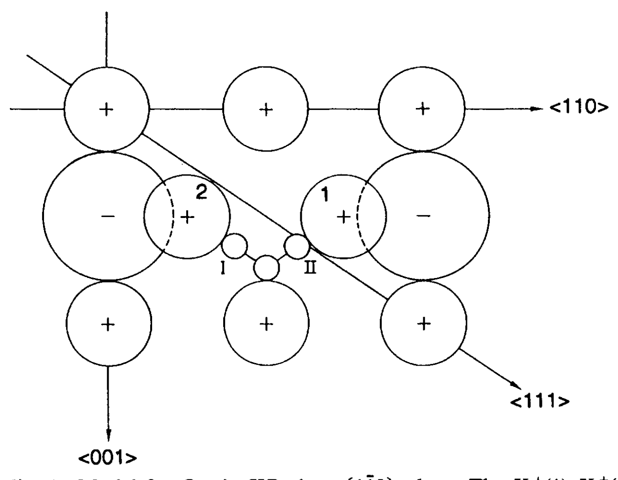

Fig. 6 Model for O_3^- in KBr in a $\{1\bar{1}0\}$ plane. The $K^+(1)$–$K^+(2)$ distance is large enough to make tilting of the ozonide ion unnecessary.

Conclusion

In KCl an O_3^- ion with a peculiar g-tensor behaviour has been studied by EPR. We tentatively propose a single vacancy model wherein the O_3^- ion is treated as a three-dimensional structure fitting as close as possible between five of the six nearest K^+ neighbours. Because of the larger interatomic distances in KBr, such an arrangement is possible without tilting, whereas in KCl at the lowest temperatures such a configuration is only possible by tilting the molecular ion in a $\{1\bar{1}0\}$ plane. By raising the temperature the ozonide ion gets gradually more squeezed by the surrounding ions, increasing g_y and g_z. However, this model should be checked by detailed calculations.

Also ENDOR measurements are currently being carried out in order to check for the possible presence of an accidental impurity causing the tilting angle and the positions of the surrounding K^+ ions. Finally the temperature behaviour of the g-tensor seems an interesting subject for further theoretical work.

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