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EXPERIMENTAL RESULTS ON A NEW O_2^- CENTER IN CaF_2 CRYSTALS ⁽¹⁾, ⁽²⁾

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Résumé. — Ce travail donne le modèle d'un centre O_2^- perturbé observé dans des fluorines naturelles. Ce modèle a été déduit des expériences d'absorption optique, d'effet Raman et des mesures RPE et ENDOR. Une bande d'absorption optique de ce centre est observée dans le visible. Elle présente une structure vibronique permettant de déterminer l'énergie de vibration interne du O_2^- dans son état électronique excité. Le quantum d'énergie est de $900 \pm 30 \text{ cm}^{-1}$. L'énergie de vibration de l'état fondamental a été déterminée à partir des mesures Raman. Son quantum est de $1\,038 \pm 2 \text{ cm}^{-1}$.

Abstract. — The model of a perturbed O_2^- center in CaF_2 is discussed on the basis of results from optical absorption, resonant Raman scattering, EPR and ENDOR measurements. Compared to the unperturbed center [4] the optical absorption of the presently discussed one is shifted to the visible and it exhibits a multiphonon structure. The O_2^- stretching mode energy in the electronic excited state deduced from this structure is found to be 900 cm^{-1} . A resonant Raman effect is observed up to 2nd order yielding the vibrational energy in the electronic ground state. The determined value amounts to $1\,038 \text{ cm}^{-1}$. The Raman selection rules are consistent with a molecular vibration along $[1, 0, 0]$.

The ENDOR data are coherent when the center is assumed to be located near a fluorine cube edge probably substituting for two F^- ions. At room temperature the center exhibits an orthorhombic g tensor in EPR. At higher temperatures, however, motional effects show up. The EPR spectrum becomes axial indicating vibrational motion of the center.

The O_2^- molecule ion incorporated into the alkali halide crystals has first been identified by Känzig and Cohen [1] by using EPR technique. At present this center represents a well investigated system ([2], [3] and others) and its preparation in a controlled manner is essentially known.

The alkaline earth fluorides do not show this center when the usual preparation methods are applied. Invariably the oxygen enters as O^{2-} into the lattice. Some natural fluorites, however, probably grown at low temperatures exhibit two kinds of O_2^- centers. The earlier identified one [4] has spectroscopic properties resembling those of the O_2^- center in the alkali halide crystals.

The other one exhibits more unusual features.

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Results concerning this center are reported in what follows. Natural crystals obtained from various donors were involved in the underlying investigations. EPR and ENDOR measurements were performed on a Varian X-band spectrometer. A Beckmann DK 2-a and an assembly built around a Zeiss monochromator were involved in the optical absorption and stress induced dichroism measurements. The Raman spectrometer consisted of a 2 watt argon ion laser, a Spex-Double-Monochromator and a photon counting detector device. All of the Raman measurements have been performed at 78 K.

The center, as deduced from the bulk of the experimental results, consists of an O_2^- molecule ion. It is located in the space left by two missing neighboring F^- ions in the fluorite lattice. The axis of the molecule ion is oriented parallel to a fourfold crystal direction. The center is probably associated with a neighboring cation vacancy located on a C_2 crystal direction perpendicular to the axis of the O_2^- molecule ion.

The maximum of the optical absorption band associated with the center is situated at approximately 2.8 eV. The spectrum presents a partly resolved vibronic structure (of the shape of a glove) due to coupling of the electronic system to the internal molecular vibration of the center. Stress induced dichroism measurements performed on this absorption band yield a separation between the peaks of $900 \pm 30 \text{ cm}^{-1}$. This value represents the energy per quantum of the internal vibration in the excited electronic state involved. Coupling of the center to the lattice is rather strong leading to a near gaussian shape of the individual « fingers » in the absorption spectrum.

Some Raman measurements have been performed on this center in order to investigate on the following points :

— Orientation of the internal local vibration of the O_2^- with respect to the crystal axes.

— Frequency of the ground state internal vibration.

Raman spectroscopy had to be applied to answer the second point since no fluorescence associated with the center could be detected.

When light of the laser was shined into the optical absorption band of the center two Stokes Raman scattering lines were observed. They are situated at a distance of $1\,038 \pm 2 \text{ cm}^{-1}$ and $2\,076 \pm 6 \text{ cm}^{-1}$ from the line due to the incident and Rayleigh light.

The first one of the Raman peaks corresponds to the excitation of one vibrational quantum and the second one is associated with two quanta. The integrated intensity of each of the two lines is of comparable magnitude. This is to be expected as both are explained by resonant Raman scattering in second order time dependent perturbation theory. Since a Stokes shift and a change of vibrational frequency are involved by going from the ground to the excited electronic state the vibrational wavefunctions of the two electronic states considered are not mutually orthogonal leading in the Condon approximation to multiphonon lines in the same order of approximation as the one phonon Raman line.

The polarization measurements performed on the Raman lines yield the internal vibration to be oriented along a fourfold crystal axis. The alignment of the polarization device has been checked by using the T_{2g} optical phonon Raman line of the CaF_2 crystal matrix situated at $324 \pm 2 \text{ cm}^{-1}$.

The frequency of the internal vibration of the center in its electronic ground state is of magnitude comparable to the same quantity of the O_2^- molecule ion in the alkali halides. The optical absorption band, however, is strongly shifted towards longer wavelengths with respect to the usually observed position. This shift is attributed to a much stronger ligand field acting upon this center, compared to the cases of the O_2^- molecule ion in the alkali halides or the other O_2^- center in CaF_2 .

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