ANISOTROPY OF THE ELECTRON DENSITY AND EFFECTIVE CHARGE IN ALKALI HALIDE MONOCRYSTALS

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We discuss the use of the positron annihilation method to study the electron structure of alkali halide monocrystals, particularly the electron density and the effective charge of the ions. The distribution of electron density and the values of the effective ion charge are found experimentally for two crystallographic directions, ⟨110⟩ and ⟨100⟩, in a KBr monocrystal. On the basis of the data obtained it is concluded that this is an effective method for obtaining information about the anisotropy of electron states in the crystal.

In studying the nature of the chemical bond in solids it is important to determine the instantaneous and time-averaged distribution of the electron density, together with the effective charges, dimensions, and polarization properties of the ions due to the influence of the neighboring ions. These data provide a scientific basis to the search for materials with given properties, which is of particular value to research, for example, in the area of quantum electronics. The best developed methods from which it is presently possible to obtain sufficiently reliable data about the distribution of electron density in a crystal are those of x-ray, electron, and neutron diffraction analysis. The common drawback of these methods is the difficulty of processing the experimental data and the complexity of the equipment used in the experiments.

In recent years the use of positrons to investigate the electron structure of solids and liquids has begun to be popular. Positrons entering a material substance are rapidly slowed to thermal velocities and then undergo annihilation with the valence electrons, which have energies (1-10 eV) much higher than the kinetic energy of the positrons. The motion of the valence electrons leads to the blurring of the spectrum line of annihilation radiation; this motion depends on the form of the momentum distribution function of the valence electrons \( \rho(p) \), which is related to the experimentally measurable angular distribution of the annihilation photons \( N(\Theta) \) by the expression

\[
N(\Theta) = A \int_0^\infty \rho(p) p \, dp,
\]

where \( A \) is a constant that takes into account the experimental geometry, and \( p \) is a component of the electron momentum. From Eq. (1) we find

\[
\rho(p) = \frac{1}{A} \frac{dN(\Theta)}{d\Theta}.
\]

From \( [1, 2] \) we know that \( \rho(p) \) is proportional to the absolute squares of the Fourier-transformed resultant electron and positron wave functions, i.e.,

\[
\rho(p) = \text{const} \sum_j \left| \int e^{-i\mathbf{k}\cdot\mathbf{r}} \psi_j^* \gamma_+ d\tau \right|^2,
\]

where \( \psi_j \) is the wave function of the \( j \)-th electron and \( \psi_+ \) is the positron wave function. Thus from Eq. (3) we can obtain the quantity \( |\psi_j^* \psi_+|^2 \), which gives the distribution of electron density in the crystal.

Earlier studies for various alkali halide crystals have shown that in each case for fluorides and chlorides, the magnitude of the electron-positron wave function for the external electrons of the negative ion,
Fig. 1. Angular correlation curves of annihilation photons in a KBr monocrystal: 1) with the \{100\} plane parallel to the axis of the annihilation detector; 2) with the \{110\} plane parallel to the axis of the annihilation detector.

Fig. 2. Slope of the angular correlation curves of annihilation photons in a KBr monocrystal (see text).

 obtained from Eq. (3), is similar to the Hartree–Fock wave functions for a free ion \([2, 3]\). For these crystals the resultant wave function and the wave function of the free-ion electrons give a distribution of electron density in agreement with the data obtained from x-ray diffraction analysis. Since the measurements in \([2, 3]\) were performed in polycrystals, it is clear that the results give some averaged electron density unrelated to any specific crystallographic directions. Recently the influence of monocrystal orientation on the form of the angular correlation curves for annihilation photons has been observed \([4-6]\). Thus the method of positron annihilation makes possible a more accurate picture of the electron structure of a monocrystal, and in a manner that is simpler and easier than that provided by the other familiar methods.

The difference in the electron density depending on the monocrystal orientation is particularly significant for particles that are “channeled” through the monocrystal along a chain of ion rows. In this case the particles do not experience elastic nuclear collisions, and the primary cause of their braking is the loss of energy by ionization in close and distant (resonance) collisions with the electrons in the shells of the atoms or ions of the lattice \([7]\). For fast channeled particles the portions of energy loss in close and in distant collisions are approximately equal. For channeled slow particles the primary contribution to the total energy loss comes from the collective excitation of valence electrons. It was shown in \([8]\) that the energy loss from charged particles to the valence electrons, apart from the loss to collective (plasma) excitations in which all the valence electrons participate, also includes the excitation of the local density of valence electrons in the lattice channels through which the trajectory of the charged particle passes. In both cases the braking of the channeled particles must be sensitive to changes in the electron density in the crystal.

In the present work we obtain experimentally the distribution of electron density and the value of the effective charge of the Br\textsuperscript{−} ion in two crystallographic directions, \(\langle 100 \rangle\) and \(\langle 110 \rangle\), from the angular correlation curves of annihilation photons in a KBr monocrystal. In our experiment we used the experimental apparatus described in \([9]\). The measurements of the correlation curves for the KBr monocrystal were performed first; they confirmed the basic laws observed earlier for other alkali halide crystals \([4]\).

Figure 1 shows the angular correlation curves of annihilation photons in a KBr monocrystal, normalized to unit area. Curve 1 corresponds to the annihilation of positrons in a monocrystal whose \{100\} plane lies parallel to the axis of the annihilation detector. Curve 2 corresponds to the case in which the \{100\} plane lies at an angle of 45° to the measurement axis. A comparison of the resulting distributions shows a notable difference in the shape of the curves; the half-width of curve 2 is 8% larger than that of curve 1. Thus we have detected a dependence of the angular distributions on the choice of the crystallographic direction in the KBr monocrystal.

As Eq. (3) indicates, in order to obtain information about the electron density distribution we must take the derivative of the experimentally determined angular distribution function of the annihilation quanta, \(N(\theta)\), with respect to the angle \(\theta\). The curves thus obtained are shown in Fig. 2 for the two crystallographic directions respectively; their shape is well approximated by the function \(\kappa \cdot \exp\left(-\kappa^2/2\alpha\right)\), where