DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-77/02
January 1977

Investigation of the Phonon Broadening of Core Levels in NaCl

by

M. Iwan
II. Institut für Experimentalphysik der Universität Hamburg

C. Kunz
Deutsches Elektronen-Synchrotron DESY, Hamburg

Abstract

We have investigated the temperature dependence of the Na^+-2p-photoemission linewidth from thin films of NaCl. We found a large contribution to the linewidth due to coupling to lattice vibrations. Widths of the Na^+-2s, Cl^--3s, Cl^--2p lines are given at T = 300 K.

2 HAMBURG 52 · NOTKESTIEG 1

To be sure that your preprints are promptly included in the
HIGH ENERGY PHYSICS INDEX ,
send them to the following address (if possible by air mail) :

DESY
Bibliothek
2 Hamburg 52
Notkestieg 1
Germany

Investigation of the Phonon Broadening of Core Levels in NaCl

M. Iwan

II. Institut für Experimentalphysik, Universität Hamburg, 2000 Hamburg 50

and

C. Kunz

Deutsches Elektronen-Synchrotron DESY, 2000 Hamburg 52

We have investigated the temperature dependence of the Na^+-2p-photoemission linewidth from thin films of NaCl. We found a large contribution to the linewidth due to coupling to lattice vibrations. Widths of the Na^+-2s, Cl^--3s, Cl^--2p lines are given at T = 300 K.

It was already recognized in the early days of XPS experiments that the width of core lines in alkali halides is considerably larger than the Auger width. Citrin et al.[1] and Matthew and Devey[2] have given an explanation of that width in terms of the excitation of optical phonons. In a simple minded approach phonons appear to be unimportant for core electron excitations since the lattice motion is slow compared to the excitation process. A closer view at the total wavefunction of the ground state and the excited state, however, reveals that the ground state lattice zero point oscillation or motion at finite temperatures is reflected through the Franck-Condon principle in a width of the UPS line. Figure 1 shows this in a simplified picture which gives schematically the energy of the initial and final states as a function of a configuration coordinate q, e.g. the Cl^- nearest neighbor distance. The relaxation energy E_R can be calculated from the electron-LO phonon interaction Hamiltonian:[1,3]

$$E_R = e^2 \left(\frac{6}{\pi V}\right)^{1/3} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right) \qquad (1)$$

where ε_∞ is the dynamic, ε_0 the static dielectric constant, V the volume of the primitive lattice cell. This yields E_R = 1.73 eV for NaCl. The electronic transitions occur into the steep part of the final state potential curve at fixed q. In different cells in the sample or at different times the lattice is either contracted or expanded or in a state in-between. Therefore different numbers of phonons are excited in the final state (the average number depends on the so-called Huang-Rhys factor[4] $E_R/\hbar\omega_{LO}$, where ω_{LO} is the longitudinal optical phonon frequency). The phonon broadening is reflected in the spectrum of the UPS core line. The individual phonon lines are usually not resolved because of their narrow spacing ($\hbar\omega_{LO}$ = 33 meV for NaCl) and because of a smearing due to dispersion. The FWHM (full width at half maximum) of the lines ΔE can be expressed as[5]

$$\Delta E = 2.35 \left(\hbar\omega_{LO} E_R \coth \frac{\hbar\omega_{LO}}{2kT}\right)^{1/2} \qquad (2)$$

We have evaporated thin films of NaCl in the thickness range 36 - 240 Å in UHV with a basic pressure in the 10^{-10} Torr range onto substrate layers of evaporated clean Al films. The investigations showed that there was no thickness dependence in our thickness range. With all films charging was negligible at temperatures $\geq$ 300 K. At LNT (liquid nitrogen temperature) only with the 36 Å film charging was negligible.

Synchrotron radiation from the 7.5 GeV synchrotron at DESY was monochromatized in the range 20 - 290 eV by a specially designed grazing incidence monochromator.[6] The electron analyzer was of the spherical type. Although investigations were performed at several photon energies the result of the temperature dependence as shown in Fig. 2 was obtained with 60 eV photon energy and a joint resolution of the monochromator and electron analyzer of 0.3 eV.

The theory according to Eq. (2) is compared with the experimental results in the temperature range LNT - 660 K in Fig. 2. The experimental results are plotted without corrections for the instrumental resolution of 0.3 eV and without corrections for the spin orbit splitting of 0.17 eV of the two levels $2p_{1/2}$ and $2p_{3/2}$. These effects were estimated to contribute only about 16 % to the total width. The experimental width of the Na^+-2p UPS core line, however, is about 0.5 eV larger than the theoretical one and has a slope as a function of temperature which is equal to the predicted one. The measured changes of the line width agree with the calculated changes within 0.03 eV.

Additionally we have measured the width of all UPS core lines in NaCl in the range of photon energy of our monochromator.[5] The results, including the binding energy E_B, the FWHM, the width of the resolution function and the width corrected by quadratic resolution are given in Table 1. There appears to be no significant difference between the width of the Na^+-2p and the Cl^--2p lines. The Na^+-2s and the Cl^--3s lines obviously have a remarkable contribution to the width from the Auger decay.

Table 1: Binding energies (E_B) relative to the top of the valence band and FWHM of core level photoemission lines at room temperature from 70 Å thick NaCl films. The data for the Cl^--2p line were obtained with a 240 Å thick film. The last column gives a corrected FWHM (quadratic subtraction of the resolution function)

Core level	E_B (eV)	exp. FWHM (eV)	FWHM (res.fct.) (eV)	FWHM (corr.) (eV)
Cl^--3s	13.0±0.2	2.3±0.1	0.9	2.1
Na^+-2p	27.3±0.2	1.25±0.05	0.3	1.21
Na^+-2s	60.4±0.2	2.1±0.1	0.6	2.0
Cl^--$2p_{3/2}$	196.2±0.3	1.7±0.3	0.7	1.55
Cl^--$2p_{1/2}$	197.8±0.3	1.6±0.3	0.7	1.44

We include that the theory as given by Eq. (2) appears to be qualitatively correct. The difference in the absolute magnitude of the broadening can have many reasons. The theory if definitely oversimplified in using the Born-Oppenheimer approximation,[5] in assuming the same phonon frequency for the excited and the ground state and in neglecting any dispersion of the LO phonon frequencies. Model calculations by Matthew and Hart-Davis[7] on one-dimensional chains, taking a quantum statistical average over all oscillation modes in the linear approximation, give values for $(\Delta E)^2$ which are 20 % larger than in the Einstein model. Further, surface modes are not considered which might contribute to the width. We want to stress that our resolution is much better than in the measurements of Citrin et al.[1] on the potassium halides. We therefore do not depend on deconvolution procedure for the extraction of our results.

Recently Sunjic and Lucas[8] tried to calculate the influence of the finite lifetime of the hole due to Auger decay on the width of the UPS and XPS lines. They found a reduction of the width when the Auger width becomes comparable to or larger than $\hbar\omega_{LO}$. We do not know the Auger lifetime broadening of the 2p-hole, but we believe that it will be not less than 33 meV. Our result does not show a reduction of the theoretical width according to Eq. (2) but on the contrary a well established increase of the width.

One should , however, keep in mind that the Auger process, which is responsible for the decay of the Na^+-2p hole, here is the interatomic Auger process. An electron from the Cl^- derived 3p band falls into the Na^{2+} 2p hole and an electron from this Cl^- derived band is ejected. As a consequence the potential curve as shown in Fig. 1 exists only for a limited lifetime τ_A and after the Auger decay shifts back to another equilibrium position near that of the ground state.

Thus, when the lifetime τ_A becomes short, this will have two effects. One is the usual one, which is considered as the Lorentzian lifetime broadening of the Na^+-2p hole state. This Lorentzian should be convoluted with the distribution of individual phonon lines according to Fig. 1 and Eq. (2). Another influence on the line-shape must arise from the finite lifetime of the exited state potential curve in Fig. 1. We cannot see, however, whether this picture is identical to that on which the theory of Sunjic and Lucas[8] is based, or if not, how to proceed in a quantitative manner from it.

Literature

1. P.H. Citrin, P. Eisenberger, D.R. Hamann, Phys.Rev.Lett. 33 (1974) 965

2. J.A.D. Matthew, M.G. Devey, J.Phys. C7 (1974) L335

3. Ch. Kittel, Quantum Theory of Solids (Wiley, New York, 1963 pp. 137-142)

4. K. Huang, A. Rhys, Proc.Roy.Soc., Ser. A208 (1951) 352

5. J.J. Markham, Rev.Mod.Phys. 31 (1959) 956

6. H. Dietrich, C. Kunz, Rev.Sci.Instr. 43 (1972) 454

7. J.A.D. Matthew, A. Hart-Davis, Phys.Rev. 168 (1968) 936

8. M. Sunjic and A. Lucas, to be published in Chem.Phys.Lett.

Figure Captions

Fig. 1 Configuration diagram showing the ground state at the equilibrium position q_o and the doubly ionized state of Na^{2+} in NaCl. A band of phonons around the n^{th} phonon state is excited after the photoelectron has left the lattice site.

Fig. 2 Temperature dependence of the Na^{+}-2p photoemission line width ΔE.

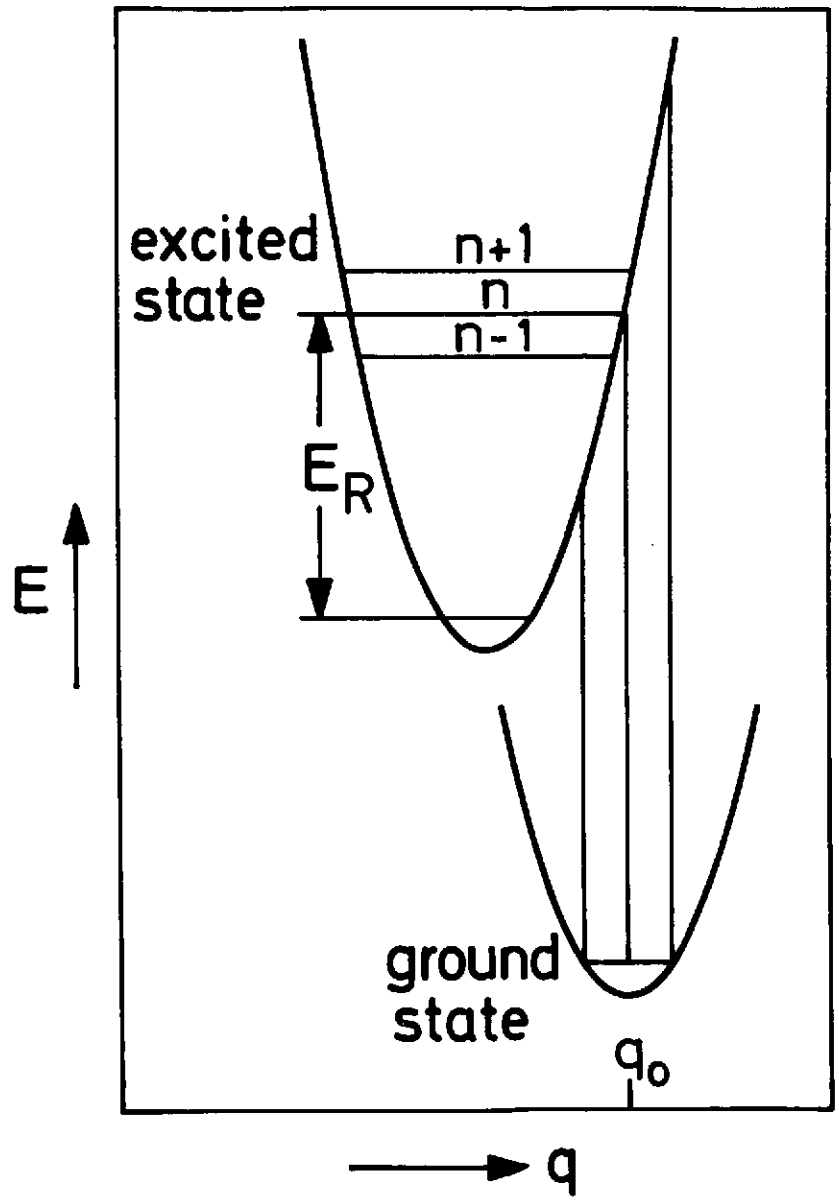

Fig. 1

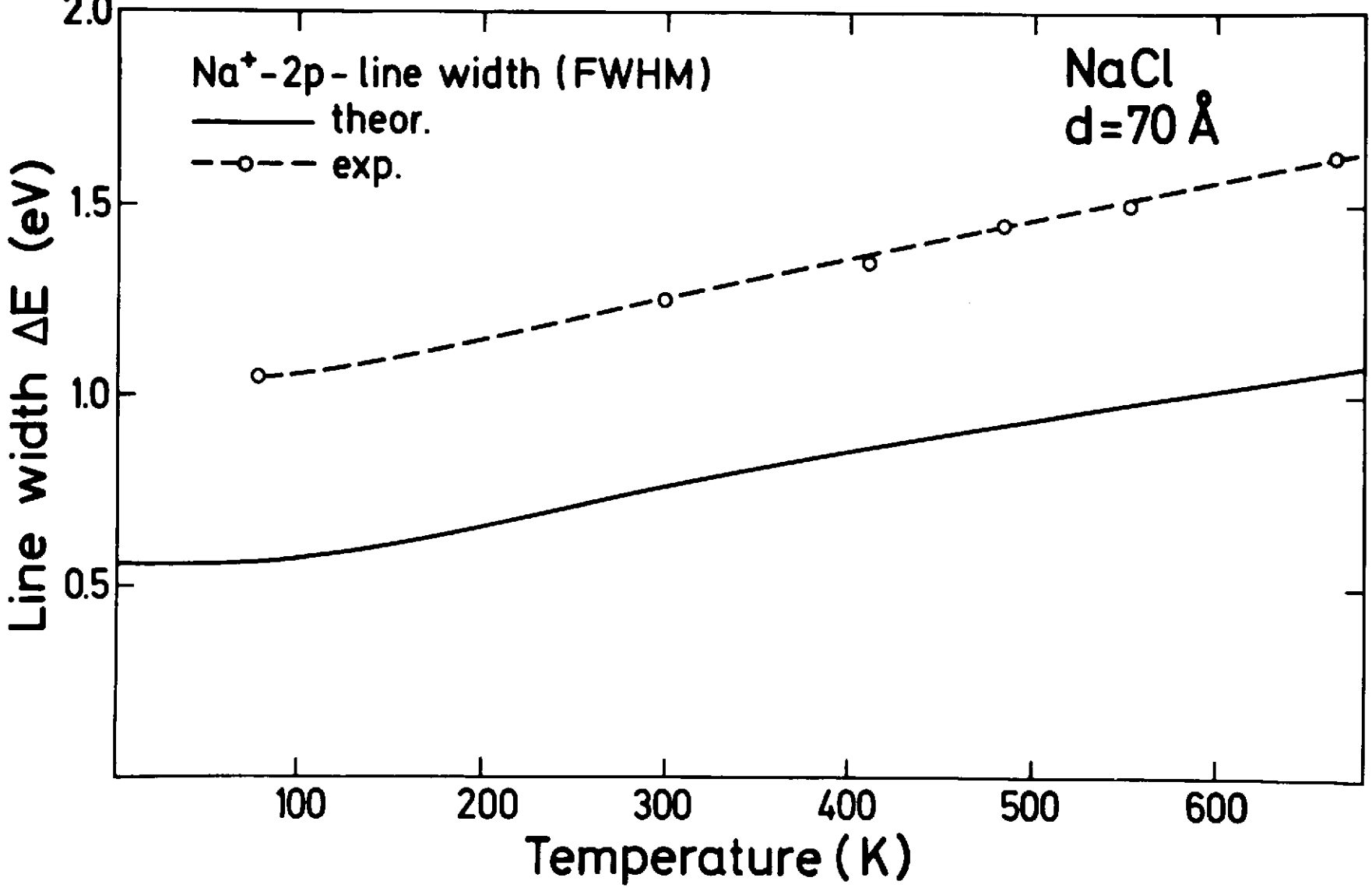
Na+-2p-line width (FWHM)
theor.
exp.
NaCl
d=70 Å
Line width ΔE (eV)
2.0
1.5
1.0
0.5
100
200
300
400
500
600
Temperature (K)

Fig. 2