Spectroscopy with Phonons on $Al_2O_3:V^{3+}$ Using the Phonon Bremsstrahlung of a Superconducting Tunnel Junction

H. Kinder

Institut für Festkörperforschung, Kernforschungsanlage Jülich, Jülich, Germany

(Received 10 April 1972)

The sharp edge of the phonon "bremsstrahlung" spectrum of a superconducting tunnel junction was isolated by modulation. This yielded a monochromatic, voltage-tunable phonon source which was applied for phonon spectroscopy on V^{3+} ions in Al_2O_3. At a frequency corresponding to the ground-state splitting of V^{3+} an absorption dip was obtained due to resonant scattering. A frequency resolution of about 3% of the energy gap was achieved.

In 1967 Eisenmenger and Dayem[1] used a symmetric superconducting tunnel junction as a source of monochromatic phonons in the range above 100 GHz. The phonons originate on recombination of quasiparticles which are excited in the junction by single-particle tunneling. Though this is a promising device in a frequency range previously inaccessible, except by thermal phonons, only a few applications have so far been proposed. This is mainly because the recombination process produces phonons at a fixed frequency equal to 2Δ, the energy gap of the superconductor. Tuning the energy gap was attempted by Narayanamurti and Dynes using a magnetic field.[2] In the presence of a magnetic field the density of states is smeared out, however, so that a substantially broadened spectrum of emitted phonons was observed. In addition the detector sensitivity decreases rapidly on lowering the mean energy gap. Therefore this method does not appear to be readily suitable for phonon spectroscopy.

In this Letter, we present a new method which relies on the phonon "bremsstrahlung" of the superconducting junction, rather than on the recombination radiation. A monochromatic source of phonons is obtained which can be tuned simply by adjusting the battery voltage. Using this source we demonstrate the feasibility of quantitative phonon spectroscopy with V^{3+} impurities in sapphire.

Following single-particle tunneling at a voltage exceeding 2Δ, the quasiparticles attain a continuous energy distribution up to a maximum energy $E_M = eV - \Delta$. These "fast" quasiparticles will decay before recombination, being gradually slowed down by phonon emission. Thus a continuous phonon spectrum is generated with a maximum frequency given by $\omega_M = (eV - 2\Delta)/\hbar$. We call this the "phonon bremsstrahlung spectrum" (PBS) of the junction in analogy with the x-ray bremsstrahlung spectrum generated by fast electrons. The PBS exhibits a discontinuous edge at the maximum frequency ω_M which is mathematically due to the confluence of two BCS square-root singularities. This was demonstrated in a previous communication[3] which was based on theoretical work by Tewordt.[4] The simplified two-level model proposed by Dayem, Miller, and Wiegand[5] does not reproduce the step edge.

In order to obtain a monochromatic phonon source we make use of this sharp edge. This is possible in view of the unique voltage dependence of the PBS: A small change in the voltage (i.e., a modulation) will shift the edge while leaving the rest of the spectrum essentially unaffected. This is shown quantitatively in Fig. 1. The upper traces show the spectral intensities of the phonon bremsstrahlung spectra, $N(\omega, V)$, calculated as before[3] for a set of voltages. The differential

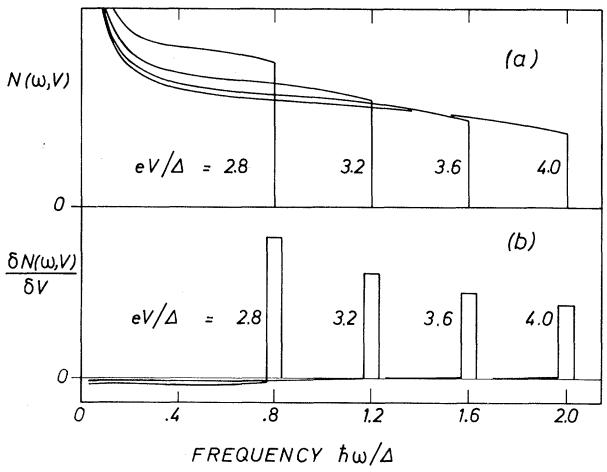

FIG 1. (a) Voltage dependence of the calculated PBS. (b) Differential PBS resulting from voltage modulation. Rectangular peaks are used to represent δ functions of corresponding strength. Their width is artificially adapted to the experimental result.

spectrum $\delta N(\omega, V)/\delta V$ is also plotted for each given voltage. A finite δV is used to show the area of the ideally δ-function-shaped peaks at ω_M. Only a very small, smooth contribution (visible in the trace for $V = 2.8\Delta$) is found at frequencies below ω_M. Thus the differential PBS is highly monochromatic and tunable by adjusting the voltage. The actual linewidth of our source is expected to be equal to the width of the sharp current rise at 2Δ in the I-V characteristic of the generator since this property involves the same convolution of densities of states. This width is a few percent of 2Δ for most materials.

The frequency range of the device extends up to $2\Delta_G$, the generator gap frequency, since reabsorption within the generator comes into play, resulting in the breakup of higher-frequency phonons. This process was described in our previous paper[3] and was also confirmed by Dynes, Narayanamurti, and Chin[6] for tin. A lower limit to the range available for spectroscopy is imposed by $2\Delta_D$, the detector gap when a tunnel junction is used as detector.[1]

In order to demonstrate the capability of this new method, we investigated V^{3+} ions in sapphire. These have an electronic ground state split by spin-orbit coupling by about 8 cm^{-1} (250 GHz), as measured by microwave[7] and far-infrared[8] techniques. The associated resonant phonon scattering was originally seen in heat-conductivity measurements.[9] In fact, $Al_2O_3:V^{3+}$ serves as a test substance for phonon experiments.[10,2] For a spectroscopic investigation of the resonant scattering by our new method, we conveniently used a symmetric tin junction as the generator; impure aluminum was chosen for the detector to cover a frequency range from about 150 to 280 GHz.

The experimental arrangement is shown in Fig. 2. The generator frequency ω_M is determined by a dc voltage which is swept very slowly. The differential spectrum is extracted by modulation using small pulses of constant amplitude and about 200 nsec duration. This time resolution is used to separate the different phonon polarizations by time of flight. Electromagnetic feed through is ruled out since it is constant during the measurement. No additional ac modulation is necessary. We have eliminated by regulation the nonlinearity of the detector junction, which is due to a shorter recombination lifetime[11] at higher phonon injection rates. The latter effect was described in detail by Dayem, Miller, and Wiegand.[5] A constant lifetime is imposed by monitoring the density of quasiparticles in the

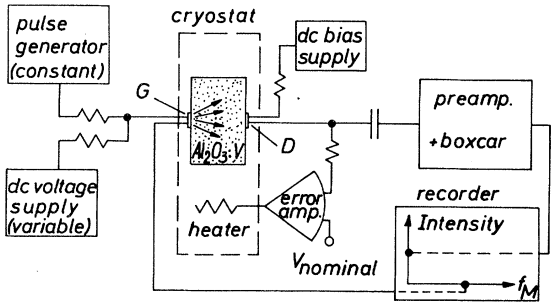

FIG. 2. Schematic diagram of the experiment. G is the generator junction (Sn-oxide-Sn); D is the detector (Al-oxide-Al).

detector using the dc tunneling current at the operating point. A dc deviation of the operating point from the nominal voltage causes a temperature change which automatically restores the quasiparticle density.

As a result only the small time-varying component of the phonon intensity causes a shift of the operating point which actually constitutes the response of the detector to the differential spectrum. This response signal is amplified and fed to a boxcar integrator for selection of the proper phonon pulse. Thus we obtain on the recorder the differential intensity of phonons injected into the detector as a function of their frequency ω_M. The latter is obtained from the generator voltage by subtracting $2\Delta_G$ as measured from the tunneling characteristic.

The results obtained with samples of sapphire 6 mm long and 10 mm in diameter, containing 200 ppm V ions, are shown in Fig. 3. Three dif-

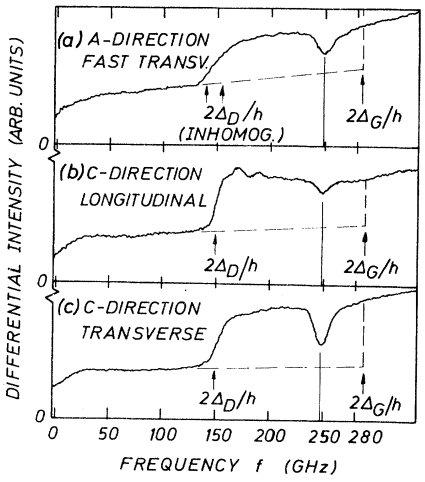

FIG. 3. Differential intensity of detected phonons as a function of the frequency $f_M = (eV - 2\Delta_G)/h$. All measurements at 1.02···1.05 K.

ferent phonon modes have so far been investigated. At lower frequencies, all traces only exhibit the background of recombination radiation. Above the detector gap frequency the phonons due to the differential PBS manifest themselves through an increase in intensity. The sharpness of the increase is determined mainly by the homogeneity of the aluminum films used for the detector. In the top trace, for instance, the aluminum films were strongly nonuniform. This, of course, does not affect the linewidth of the differential PBS.

At about 250 GHz we obtain a prominent dip in all samples doped with V, which is absent in pure sapphire. This is clearly due to resonant scattering of the V^{3+} ground state. To measure the frequency accurately, we have to determine the proper origin of the frequency scale. For reasons similar to those given for the linewidth, one should set the zero at the voltage of the inflection point at 2Δ in the I-V characteristic of the generator. The frequency of the dip minimum was then found to be 248 GHz (8.27 cm^{-1}) for all our measurements, although the actual gap voltage differed slightly from sample to sample. Our value coincides with the results of Vinogradov *et al.*[7] (248 GHz) and agrees with the value of Joyce and Richards[8] (8.25 ± 0.2 cm^{-1}), but disagrees with the result of Arnold, Smith, and Mires[12] (8.06 cm^{-1}), obtained by magnetic susceptibility measurements.

The depths of the dips obviously vary for the different phonon modes. Estimating the background of recombination phonons by extrapolation, one may deduce from the intensities of the dip minima the coupling parameters of the $\Delta M = 1$ transition. For longitudinal phonons propagating in the c direction the coupling should be forbidden.[10] We observe, however, a finite absorption. This may be partly due to slightly off-axis phonon paths allowed by the finite areas of the junctions (1.5×1.5 mm^2). However, it is hard to account for the full magnitude of the observed absorption dip solely by means of this effect. In the a direction we find an almost equal coupling strength in preliminary measurements on longitudinal phonons.

From the half-width of the observed dips we may obtain an upper limit for the linewidth of our phonon source. In the case of weak absorption, as in Fig. 3(b), one can deduce the half-width directly. In the case of strong absorption the full exponential dependence of the intensity on the absorption coefficient must be taken into account in order to obtain the true half-width. In this way we obtain the same half-width for all phonon modes, 55 μeV (13 GHz) within experimental error. The actual linewidth of the phonon source should be smaller than the observed one as a result of the finite width of the V^{3+} absorption. Taking a width of $\simeq 0.3$ cm^{-1}, as measured by Joyce and Richards,[8] and assuming Gaussian line shapes, we obtain $\simeq 9$ GHz or 3% of $2\Delta_G$ for the half-width of the differential PBS. We have already used this value for the plots in Fig. 1(b).

The trace in Fig. 3(b) exhibits small oscillations above $2\Delta_D$. These were indentified as thickness resonances (standing waves) in the detector, which are successively excited as the frequency increases. The structure is much more pronounced, and wider spaced, for thinner films and has some interesting implications which we shall report elsewhere.

To obtain a confirmation of the cutoff at $\hbar\omega_M = 2\Delta_G$, we investigated the time of escape from the generator junction. This turned out to be larger for the recombination phonons ($\hbar\omega_M < 2\Delta_D$) than for the PBS phonons ($2\Delta_D < \hbar\omega_M < 2\Delta_G$), expected in view of the longer recombination lifetime.[11] At $\hbar\omega_M = 2\Delta_G$ the time of escape again increased sharply. This shows the discontinuous onset[4] of reabsorption of PBS phonons.

In conclusion, we used the differential phonon bremsstrahlung spectrum of a superconducting tunnel junction for generating monochromatic phonon pulses which were tuned by the dc voltage. A differential power of typically 50 μW was sufficient to perform spectroscopic measurements even with the weaker longitudinal phonons, because of the high sensitivity of the detector junction in zero magnetic field. This method has opened the new field of phonon spectroscopy for quantitative experiments.

I wish to acknowledge stimulating and helpful discussions with W. Buckel, W. Eisenmenger, A. Baratoff, and H. Wühl.

[1]W. Eisenmenger and A. H. Dayem, Phys. Rev. Lett. 18, 125 (1967).

[2]V. Narayanamurti and R. C. Dynes, Phys. Rev. Lett. 27, 410 (1971).

[3]H. Kinder, K. Laszmann, and W. Eisenmenger, Phys. Lett. 31A, 475 (1970).

[4]L. Tewordt, Phys. Rev. 127, 371 (1962).

[5]A. H. Dayem, B. I. Miller, and J. J. Wiegand, Phys. Rev. B 3, 2949 (1971). The model employed in this work yields a square-root singularity at ω_M, since the high-frequency processes are qualitatively overesti-

mated by the assumption of a single final state for the quasiparticle decay, instead of a BCS density of final states.

[6]R. C. Dynes, V. Narayanamurti, and M. Chin, Phys. Rev. Lett. 26, 181 (1971).

[7]E. A. Vinogradov, N. A. Irisova, T. S. Mandel'shtam, A. M. Prokhorov, and T. A. Shmaonov, Zh. Eksp. Teor. Fiz. Pis'ma Red. 4, 373 (1966) [JETP Lett. 4, 252 (1966)].

[8]R. R. Joyce and P. L. Richards, Phys. Rev. 179, 375 (1969).

[9]B. Dreyfus and F. Zadworny, J. Phys. Rad. 23, 490 (1962).

[10]V. Narayanamurti, Phys. Lett. 30A, 521 (1969).

[11]A. Rothwarf and B. N. Taylor, Phys. Rev. Lett. 19, 27 (1967).

[12]D. J. Arnold, A. R. Smith, and R. W. Mires, Phys. Rev. B 1, 2355 (1970).

Band-Edge Excitons in PbI_2: A Puzzle?

G. Harbeke
Laboratories RCA Ltd., Zurich, Switzerland

and

E. Tosatti
Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Istituto di Fisica, University of Rome, Rome, Italy

(Received 23 March 1972)

It is shown that the exciton spectra in PbI_2 can only be described in terms of a single Wannier series with a large ground-state anomaly. This anomaly is explained by a repulsive central-cell correction due to the cationic character of the exciton.

The nature of the band-edge excitons in the layer compound PbI_2 has attracted the interest of many workers.[1-8] Originally, Nikitine *et al.*[1,2] observed an absorption spectrum with up to four lines in front of the absorption edge and explained it in terms of a Wannier exciton series $E_n = E_G - R/n^2$, with $E_G = 2.567$ eV and $R = 142$ meV at 4.2°K. It was a puzzling observation that the position of the $n = 1$ line was 82 meV higher than predicted from the formula, puzzling in view of the commonly occurring lowering of the $n = 1$ line due to central-cell corrections.[9,10] In other investigations[3,4] the $n \geq 2$ lines have not been observed and arguments have been put forward against an intrinsic origin of these lines. However, Gähwiller and Harbeke[6] later verified in reflection measurements the line structure for $n \leq 3$ on the $4H$ polytype.[11] The spectrum of the $2H$ polytype could also be fitted by a Wannier series with $E_G = 2.552$ eV and $R = 127$ meV, resulting in a ground-state deficiency of 72 meV. Recently, Baldini and Franci (BF)[7] gave a new interpretation of the observed spectra in terms of two overlapping Wannier series with identical binding energies of 55 meV and a separation of 24 meV. These two series would originate from a split upper valence band, transitions from the higher of the two being allowed for $\vec{E} \perp \vec{c}$ which is the actual configuration in the previous measurements. Transitions from the lower sub-band would be allowed only for $\vec{E} \parallel \vec{c}$ and would appear in the $\vec{E} \perp \vec{c}$ data because of finite-aperture effects or because of relaxation of the selection rules through phonon participation. Here we report new experimental evidence which disproves the BF interpretation. We further present an estimate of a repulsive central-cell correction which explains the observed ground-state deficiency and allows a consistent picture of the nature of the band-edge excitons in PbI_2.

Some evidence against the double-series interpretation can already be found in the published data for $\vec{E} \perp \vec{c}$. In fact, the integrated intensity ratios of the first two lines obtained from absorption[1] and reflectivity[6] measurements, taken in different setups on the $2H$ or $4H$ polytypes, are always 13 ± 2 which would be unlikely on the hypothesis that a finite aperture gives rise to the second line. The value of 13 is not far off from the theoretical value of 8 for a hydrogenlike single series. On the other hand, the observed intensity ratio of the first to the third line (I_1/I_2 in the BF interpretation) is as large as about 70, much too far from 8.

The crucial experiment to check the BF interpretation is a measurement of an $\vec{E} \parallel \vec{c}$ spectrum in which then the first peak should disappear and the second peak should strongly increase. Pre-