fields where Eq. (1) is expected to break down.[13]

The present measurements of the low-temperature limit of the specific heat of a typical Kondo system thus not only suggest a choice between various theoretical models, but also yield important conclusions concerning the entropy of the very low-temperature state of the system.

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[10] Contributions to the impurity specific heat arising from mechanisms other than the Kondo effect can be estimated to be smaller than the precision in the present data. For example, at 37 mdeg K the inverse T^2 specific heat of 20 copper nuclear quadrupole moments Q in the effective electric field gradient eq produced by Fridel oscillations around the iron impurity contributes only about 0.13×10^{-3} J/mole Fe K, taking $q=5\times10^{23}$ cm^{-3}, the largest value estimated for this quantity by Kohn and Vosko [Phys. Rev. 119, 912 (1960)] for nonmagnetic impurities in copper. This contribution increases by less than an order of magnitude even if the Friedel screening is provided entirely by resonant d-wave scattering. The limited Au^{197} Mössbauer line broadening seen in the related Au$_{95}$Fe$_5$ alloy system also indicates that the nuclear quadrupole effect is quite small. [U. Gonser, R. W. Grant, C. J. Meechan, A. H. Muir, Jr., and H. Wiedersich, J. Appl. Phys. 36, 2124 (1965), and A. H. Muir, Jr., private communication.] Other unanticipated contributions to the measured impurity specific heat cannot be completely ruled out.

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CONDUCTION-BAND STRUCTURE IN ANTHRACENE DETERMINED BY PHOTOEMISSION

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The structure of the conduction-band system of crystalline anthracene has been investigated by means of electron photoemission from negative anthracene ions formed by reaction with K and Na. A sharp emission threshold is found at 0.79 ± 0.01 eV. The lowest conduction band is less than 0.03 eV wide in agreement with the calculated value. A second conduction band, 0.3 eV wide, is also found, separated from the lower one by less than 0.05 eV.

The detailed structure of the conduction and valence bands in anthracene is of considerable interest. Both bands have been calculated to be from 0.01 to 0.02 eV wide[1,2]; charge transport in such narrow bands has been shown to result in an anomalous Hall effect, where the sign is reversed and the measured mobility much larger than the microscopic mobility.[3-5] It has also been predicted that a broader conducting state must lie above the lowest conduction band.[6,7] From the photoemission of holes from metals into anthracene, Williams and Dresner[8] established that the valence band was less than 0.1 eV wide, as predicted, and broadened by vibrational overlap. Recently, two papers have appeared describing the use of photoemission of electrons to study the conduction-band structure.[9,10] Baessler and Vaubel[9] obtained photoemission from alkali metals, yielding photoemission thresholds of 0.8 eV for Cs and 1.0 eV for Na. These were interpreted as photoemission from the Fermi level of the metal (yielding a width for the lowest conduction band approximately 0.2 eV) followed by emission into a higher band beginning 0.45 eV above the first threshold. Additional emission in the region $h\nu > 1.8$ eV was attributed to emission from a alkali metal–anthracene complex formed at the surface. Many, Levinson and Teucher,[10] studying the photoemission of electrons from Na-K alloys and various amalgams of alkali metals with Hg, found a threshold at 0.9 eV for all contacts. Their results were interpreted as emission into a broad conduction band 0.65 eV wide. A set of emission peaks at $h\nu > 1.8$ eV was attributed to four narrow conduction bands above the lower state. We believe that the interpretations made in these two papers merit further discussion. In both, the emission at higher energies coincides with the onset of triplet excitation; the four bands of Ref. 10 at 1.83, 2.01, 2.18, and 2.35 eV coincide with the triplet excitation peaks found by Avakian et al.[11] In Ref. 9, water was used as the transparent anode. The emission thresholds lie in a region of strong water absorption, as shown in curve *C* of Fig. 1, and the anode must interfere with the photoemission spectrum, at least in the case of Cs. In Ref. 10, the anode is said to be transparent to 0.83 eV but not identified.

We have studied the photoemission of electrons from well-reacted anthracene complexes with K and Na. The emission currents are one order larger than those obtained with unreacted alkali metals, enabling us to use a spectral resolution as small as 0.01 eV. The samples were cleaved from a single-crystal boule of ultrahigh-purity anthracene and etched lightly in benzene. The K electrode was deposited as a molten drop at 100°C in a nitrogen atmosphere, yielding a deep-blue interface characteristic of the K-anthracene $[K^+A^-]$ complex.[12] For Na, this was done at 135°C. The anode was a layer of D_2O, 3 mm thick, measured to be transparent for $h\nu > 0.67$ eV. Since light must pass through the crystal, its transmission was measured and is shown in curve *B* of Fig. 1. A careful check of the absorption in the region 0.76-0.85 eV for this crystal, combined with the observation that the photoemission current is always linear with incident light intensity, shows that the absorption-band peaking at 0.74 eV does not interfere with the determination of the absorption edge. It was also verified that there were no irregularities in the spectral output of the monochromator in the neighborhood of the first photoemission peak. The relative quantum yield *Y* for a crystal of 0.55 mm thick with 100 V applied is shown in curve *A* of Fig. 1. The absolute quantum yield is approximately 10^{-6} electron/photon in the range $1.1 < h\nu < 1.6$ eV.

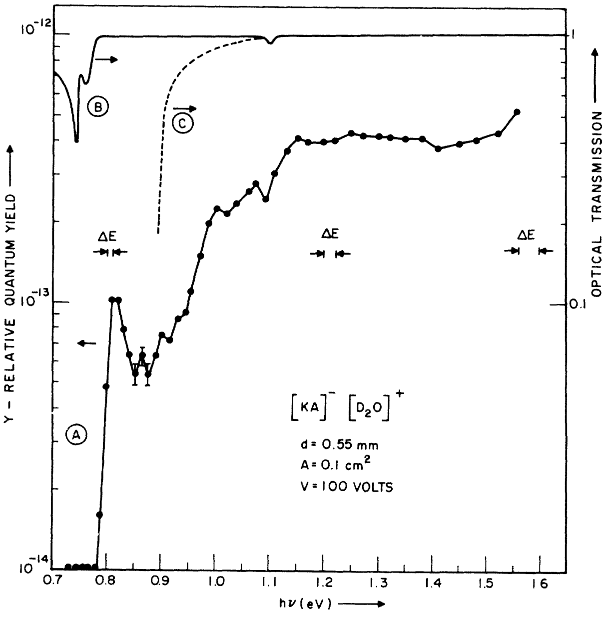

FIG. 1. *A*, Photoemission from a K-anthracene contact. *B*, Optical transmission of this crystal. *C*, Optical transmission of 1 mm of H_2O.

A sharp photoemission threshold is observed at 0.78 eV, reaching a maximum within 0.03 eV, characteristic of emission into a band of that width. The decrease in *Y* beginning at 0.82 eV can only be accounted for by a decrease in the number of initial states available, i.e., part of the emission originates in a set of surface states less than 0.05 eV wide (formed by the negative anthracene ions). At approximately 0.9 eV, a second rise in *Y* begins followed by a plateau from 1.2 to 1.6 eV. This indicates emission into a second band about 0.3 eV wide, as well as the existence of a continuum of surface states below the sharp level. For $h\nu > 1.6$ eV, *Y* rises rapidly showing the triplet structure given in Ref. 10. For the Na-anthracene contact, the shape of the emission spectrum is similar, showing a threshold at 0.79 eV and a width for the lowest conduction band of only 0.01 eV. For both contacts, a Fowler plot shows that the threshold for emission into the upper broad conduction band is separated from the top of the lower narrow band by less than 0.05 eV, rather than by 0.3 eV as predicted in Ref. 6.

It has been correctly pointed out by Mehl[13] that photoemission from the contact could not be observed if the contact is Ohmic; i_{dark} is then determined by the trapped charge and the effect of light is to change the ratio of free to trapped charge. In our case, the cathode is not Ohmic. For the crystal of Fig. 1, the curve of $i_{\rm dark}$ vs V rises rapidly in the region 400-600 V corresponding to a trap concentration of $10^{12}/{\rm cm}^3$, characteristic of crystals of this quality. At higher voltages, it follows a relation $i_{\rm dark} \propto V^{2.9}$, remaining two orders smaller than the Child's-law current to 4000 V. No evidence was found for the volume photoexcitation of trapped electrons. At the dark current level in our measurement, 10^{-10} A/cm^2, the bulk Fermi level is 0.92 eV deep. Thus, the effect is excluded on this ground, at least near the photoemission edge at 0.78 eV. Intense illumination through a Si-Ge filter, passing only $h\nu < 1.0$ eV and a Corning 7-56 filter ($h\nu < 1.5$ eV) yielded no region where $i \propto V^2$ as predicted for this effect[14] and verified experimentally[15] for volume excitation of hole traps in anthracene; rather $i \propto V^n$ where $n > 4$ was obtained.

We thus conclude that the photoemission in the region $h\nu < 1.6$ eV takes place from the contact region into the conduction-band system. The initial states are most probably the negative anthracene ions, although some emission from the Fermi sea of the metallic K cannot be excluded at higher energies. The existence of a narrow lowest conduction band is then verified, and its width, <0.03 eV, is consistent with the calculated values. A broader conduction band 0.3 eV wide lies 0.05 eV above it.

The precise correspondence of Y for $h\nu > 1.6$ eV with the triplet excitation spectrum makes it unlikely that it reflects the conduction-band structure. In some crystals, using symmetrical noninjecting H_2O electrodes, we have observed Y in the triplet region two orders smaller than in the singlet absorption (3.1 eV). When the anode is replaced with a reducing solution of Na_2SO_3 in NaOH to lower the bands at that surface,[16] Y is reduced by two orders in the triplet region but is unaffected for $h\nu < 1.4$ eV or $h\nu \geqslant 3.1$ eV. Thus, triplet excitons must be able to release holes from anode surface states. Since for triplet absorption, $\alpha = 3 \times 10^{-4}$ cm^{-1} and the exciton diffusion length $L = 2 \times 10^{-3}$ cm, the efficiency of this effect must be at least 500 times larger than for hole injection by dissociation of singlet excitons, for which $\alpha = 10^4$-10^5 cm^{-1} and $L = 10^{-5}$ cm.

When the cathode is K anthracene, Y is not affected by the nature of the anode; in this case the Fermi level at the anode lies 0.9 eV below the conduction band rather than near the middle of the energy gap, and the surface states are empty of holes. We suggest that the efficiency of triplet excitons for emptying negatively charged surface states is also very high. However, we have not succeeded in demonstrating this effect unequivocally so far.

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