Photocarrier Generation in Polysilane Films Doped With and Without Fullerene

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The photocarrier generation kinetics in poly(methylphenylsilane) films with and without C_{60} has been studied by measuring accurate subgap absorption spectra, absorption spectra contributing to photocurrent, and the normalized photoconductivity. The photoconduction spectrum of polysilane has 0.1 eV higher onset than the absorption. The photocarriers are not generated at the electrode, but in the bulk. These results suggest that the photocarriers are more likely photogenerated free-holes in a disordered system than photogenerated charged-polarons. The analysis based on a disorder model successfully explains the zero-temperature normalized photoconductivity. Doping of C_{60} sensitizes efficiently the photoconduction of polysilane in the low photon-energy region where C_{60} has optical absorption. This sensitization is suppressed at low temperatures. In the low temperature region, photogenerated holes are trapped in the tail states of polysilanes in a C_{60} doped sample and consequently, the Fermi level moves to increase the dark and photoconductivity. The trapped holes recombine with electrons from C_{60} at temperatures higher than 130 K.

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Introduction

Polysilanes are organic materials with mobility as high as 10^{-4} cm²/Vs even in unoriented films.[1] Oriented films show one order of magnitude higher mobility along the orientation and one order of magnitude less mobility perpendicular to the orientation as compared with unoriented films.[2] A possible mobility of 0.1 – 1 cm²/Vs has been pointed out for oriented films.[3,4] This anisotropy is caused by the difference in the hopping distance between the intrachain hopping and interchain hopping.[2]

The polysilane of poly(methylphenylsilane) (PMPS) shows photoconductivity and doping of C_{60} in PMPS sensitizes the photoconductivity.[5,6] It is generally accepted that C_{60} incorporated in the polysilane accepts a photogenerated electron to leave a hole in the polymer chain.[5,7] A possibility of energy transfer followed by the electron transfer from the polysilane to C_{60}, leaving a hole in the polymer chain has also been proposed.[6] It has been reported that PMPS shows a photoconduction spectrum with onset coincident with the optical absorption edge.[8,9] This measurement was done for a sandwich structure sample with a transparent electrode through which the PMPS film was exposed to light. The result has been explained by a model in which an exciton is photogenerated in the film, migrates toward the transparent electrode and dissociates, by an acceptor-like effect of the electrode, to provide a free hole.[8,9] However, this explanation is not conclusive.

It is well known that in molecular crystals, an exciton is produced by photon energies more than the exciton binding energy by 0.5 – 1.0 eV, whereupon it undergoes dissociation to produce a free hole or a free electron.[10,11] However, the situation is different in amorphous materials. The photoconduction begins almost at the optical absorption edge, which is the same in the case of PMPS. There are two models to explain this behavior. One is the disorder model,[12] that energetic disorder of hopping sites lowers the exciton binding energy. The other is the charged-polaron excitation model,[10] that photoexcitation yields charged polarons contributing to the photocurrent.

In this article, we explore the kinetics of photogeneration of carriers in PMPS films by measuring accurate subgap optical absorption spectra, subgap absorption spectra contributing to photocurrent, and the normalized photoconductivity. We also investigate PMPS films doped with fullerene C_{60}.

Experiment

Polysilane of the PMPS-type used had molecular weight of ca. 130,000. Samples of self-supporting thick films and coated thin films were prepared. The self-supporting films with thickness of 40 μm were prepared by peeling off films that were cast from a toluene solution of PMPS on mica substrates. The oriented film was also prepared by mechanically stretching the self-supporting film. The thin films were deposited onto indium tin oxide (ITO) coated glass plates by spin casting. The resulting thickness was 250 nm. The fullerene doping in the polysilane films was carried out by dissolving PMPS and C_{60} in toluene in weight ratio of 25:1. The C_{60} powder used was prepared by dc arc discharge using graphite electrodes and had a purity of at least 90%.

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For the thick samples coplanar A1 electrodes with a gap of 100 μm were prepared to avoid the acceptor-like effect of electrodes for photocarrier generation, especially in the case of oriented films that were designed for measurement of the photocurrent as a function of the orientation. On the other hand, on the thin samples, an Al electrode was deposited as a counter electrode to the ITO transparent electrode to form a sandwich cell.

Photocurrent measurements were performed with a xenon lamp as a light source, for samples kept in a temperature controlled cryostat. The parameters were the photon energy $h\nu$, temperature T, and electric field. The constant photocurrent method (CPM)[13] was also used to measure the subgap absorption contributing to the photoconduction. In this method the photon flux was measured as a function of $h\nu$, keeping photocurrent constant, namely maintaining the quasi-Fermi level for holes constant. The CPM signal or the inverse of the measured photon flux is proportional to a product of the optical absorption coefficient α and the quantum yield η. Because uniform photocarrier-generation in the bulk is a key principle, the thin samples were used for the CPM measurement. The thin samples were also used for the measurement of the electric field dependence, while the thick samples were used for other photocurrent measurements. The applied electric field was 10^4 V/cm, except for the measurement of electric field dependence. The data were taken in a pointwise manner to exclude any distortion due to residual internal space charge accumulation.

Photothermal deflection spectroscopy (PDS)[14] was performed to measure the spectrum of α in the subgap region. The samples used for this measurement were 500 nm thick films coated on quartz. The spectrum was normalized to the data in the band gap region measured by a conventional transmission method. The deflection medium used was 1,4 butanediol which does not dissolve PMPS and has a large change of refractive index with temperature ($dn/dT = 7 \times 10^{-4}$ deg^{-1}).

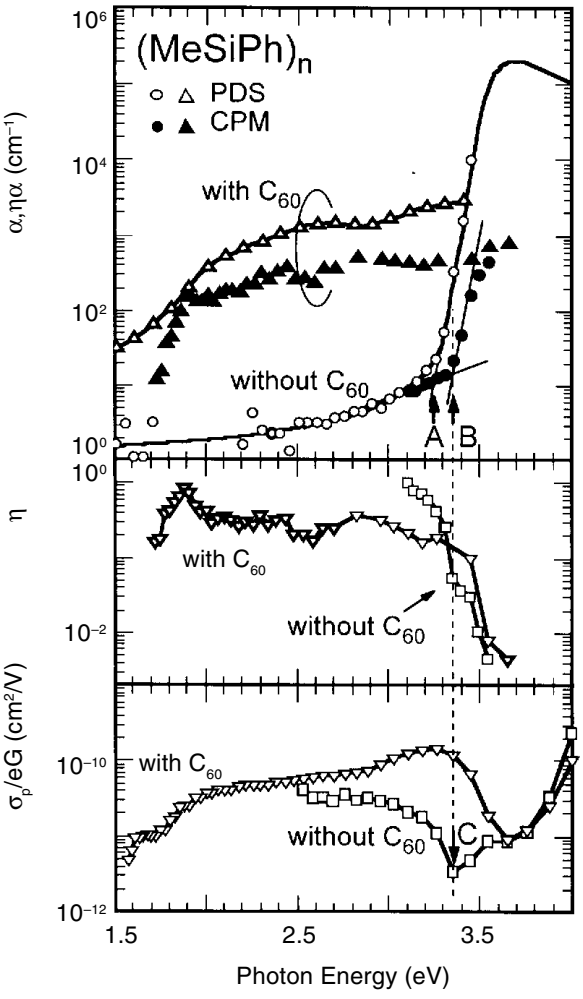

Figure 1. Spectra of the optical absorption coefficient α measured by PDS, the optical absorption contributing the photocurrent $\eta\alpha$ measured by CPM, their ratio η and the normalized photoconductivity σ_p/eG for PMPS films doped with and without C_{60}. A and B denote the onset for PDS and CPM, respectively, and C denotes the minimum of σ_p/eG. The value of η is set to be unity at a low photon energy. For CPM samples of a sandwich structure were used, while for the measurement of normalized photoconductivity samples with coplanar electrodes were used. The samples were unoriented.

Results

Figure 1 shows the spectra of α measured by PDS, $\eta\alpha$ measured by CPM, their ratio η and the normalized photoconductivity $\sigma_p/eG = \eta\mu\tau$ at room temperature for PMPS films with and without C_{60}. Here G is the excitation rate per cm^3, and μ and τ are the mobility and lifetime of carriers, respectively. The absolute value of η was not determined and is assumed for simplicity, to be unity at a low photon energy.

For the PMPS film, the PDS measurement reveals a sharp band tail with exponential rather than Gaussian distribution. The Urbach energy is estimated to be 40 meV. It also indicates quite low values of α in a low $h\nu$ region, i.e., a low density of states (DOS) in the midgap. The CPM absorption starts to rise at the point B of 3.35 eV which is 0.1 eV higher than the onset A of the PDS curve. As the photon energy increases toward 3.35 eV the η value decreases, which indicates the change of photoconduction mechanism at the onset B. This is clearly reflected by the variation of σ_p/eG measured without the acceptor-like effect of electrodes which has a minimum C coincident with the onset B. It is believed that the photoconductivity is due to impurities and/or defects at low photon energies and is dominated by the band-to-band transition at $h\nu > 3.35$ eV. The increase in σ_p/eG with increasing photon energy from the point C is caused by the increase in μ and/or τ of free holes, because the value of η does not increase. Because the current density or the carrier transport energy level in the measurement of σ_p becomes high at a high photon energy, increase in μ is most probable.

The doping of C_{60} modifies the optical absorption spectrum of the polysilane at $h\nu < 3.45$ eV. It is found that the relative value of η is high around $h\nu = 1.9$ eV and shows a steep decrease with increasing $h\nu$ from 3.4 eV. The energy 1.9 eV corresponds to the energy gap[15] of C_{60} clusters. The decrease of η is reflected in the decrease in σ_p/eG. The sensitization of photoconductivity by C_{60} is effective at photon energies up to 3.65 eV. The photocarrier generation mechanism changes to be the same as for undoped PMPS beyond this energy.

Figure 2 shows the temperature dependence of σ_p/eG measured for PMPS films. Photon energies of 3.4 ~ 3.55 eV were used in this light measurement. Photoconductivity is observed even at a low temperature of $T = 15$ K and rises steeply at $T > 200$ K. However, it decreases at $T > 240$ K. This is because of photodegradation of the

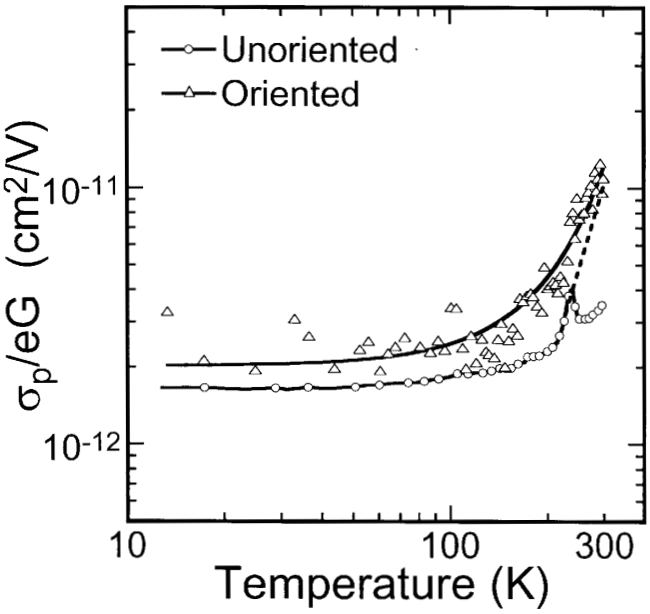

Figure 2. Temperature dependence of the normalized photoconductivity σ_p/eG for oriented and unoriented PMPS samples with coplanar electrodes. The photocurrent is measured along the orientation for the oriented film.

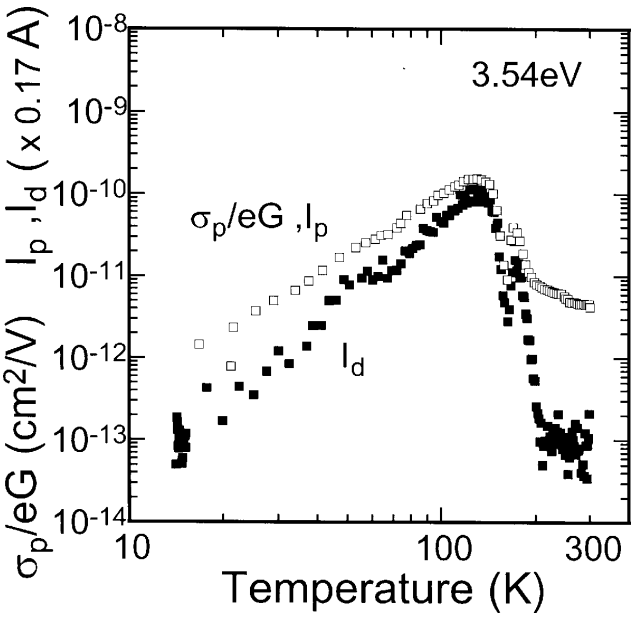

Figure 3. Temperature dependence of the normalized photoconductivity σ_p/eG, dark current I_d and photocurrent I_p for C_{60} doped PMPS samples with coplanar electrodes. The samples were unoriented.

sample. The dotted line is an expected curve. In Fig. 2, the data for the oriented film of PMPS are also plotted. This measurement was done using rather weak light to avoid the photodegradation so that the data are scattered. The value of σ_p/eG begins to rise at 100 K, which is half the value observed for the unoriented film.

Figure 3 shows the temperature dependence of dark current I_d, photocurrent I_p and σ_p/eG measured for the C_{60} doped PMPS film on 3.54 eV excitation. The value of σ_p/eG at 15 K is almost equal to the value for PMPS alone, but its temperature dependence is different. At 15 K the I_d value is ~ 10^{-13} A, which is comparable to the noise level, and the I_p value is ten times higher than the I_d value. The values of I_d and I_p, both increase with increasing temperature up to 130 K. However, this is not a real temperature dependence. We have confirmed that the dark and photocurrent increase to their respective saturated values with time even when the sample is kept at a constant temperature of 77 K. In Fig. 3, at 130 K, the I_d value begins to decrease and becomes equal to the noise level at $T > 200$ K. On the other hand, the I_p value reaches a value forty times higher than the I_p value at $T > 200$ K. In this temperature region, I_p is not thermally activated. A dip observed in I_d and I_p at 160 K is not artifactual but reproducible.

Discussion

With respect to the photoconduction spectra in Fig. 1, the free carrier generation at energies less than the absorption edge of PMPS for samples with and without C_{60} is not caused by exciton formation. Its origin in the sample without C_{60} must be other impurities and/or defects. This generation process is denoted by (1) in Fig. 4. For the C_{60} doped sample, as denoted by (2) and (3) in Fig. 4, C_{60} is photoexcited, and subsequently, an electron transfers from the highest occupied molecular orbital (HOMO) band of polysilane to C_{60} to leave a hole in the polysilane. These processes are essentially the same as reported by Kepler and Cahill.[6] In Fig. 4, HOMO and the lowest unoccupied molecular orbital (LUMO) of C_{60} are assumed to form bands because the optical absorption spectra show broad bands.

The comparison between the CPM and the PDS data for PMPS alone clearly indicates that the onset of the photocarrier generation due to the band-to-band transition is 0.1 eV higher than that of optical absorption. The correspondence of this onset with the minimum of the normalized photoconductivity measured in the cell with Al coplanar-electrodes confirms that this behavior for the photocarrier generation is characteristic of PMPS films. The evidence is inconsistent with the model proposed by Kepler and Soos[8,9] where the photocarrier generation in the sandwich cell is caused at the electrode, which acts as an acceptor to extract electrons from excitons and provide free holes.

Possible processes for photocarrier generation with low or no excess energy are a disorder model[12] for polymer materials and a model[10] of charged polaron excitation. In the disorder model for polymer materials, the energetic disorder of hopping sites in the polymer matrix lowers the dissociation energy of excitons to yield free carriers. In the charged polaron excitation model, the lowest optical transition in a one-dimensional polymer is from the ground state to the relaxed excited state which is the coupling of electrons with distortions in the polymer backbone by electron-phonon interaction. This photoexcitation yields charged (positive and negative) polarons that promptly contribute to the photocurrent without any additional energy. It is believed that the disorder model is more likely for PMPS because of the 0.1 eV excess energy. Later we will discuss the generation process of free carriers based on another approach[16] of the disorder model which has been developed in the field of inorganic amorphous semiconductors. The basic concepts in the disorder model for the polymer materials and the inorganic material are the same.

As shown in Fig. 1, the η value decreases with increasing photon energy even after the photocarrier-gen-

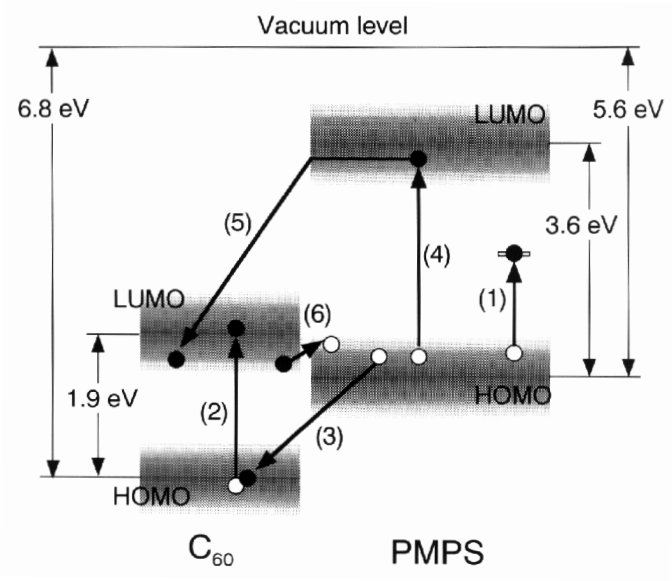

Figure 4. Scheme of generation processes of photocarriers in polysilane with and without C_{60}.

eration mechanism changes from (1) to (4) in Fig. 4. Possible origins are exciton quenching and charge trapping and recombination.

In Fig. 1 the normalized photoconductivity exhibits an increase at photon energies above 3.65 eV for films doped with and without C_{60}. This energy is higher than the peak energy of the optical absorption, indicating that the charges are photoexcited to states higher than the DOS peak. According to both the disorder models, those charges easily become free from the electron-hole pairs. The result that the sensitization of photoconduction due to C_{60} disappears at high photon energies may be caused by the low electric field, because the sensitization has a strong electric field dependence.[6]

Because of the lack of thermal energy, the value of σ_p/eG is ~ 10^{-12} cm^{-2}/V at T = 15 K, and carriers cannot hop up in energy. This value is close to the zero-temperature photoconductivity estimated for hydrogenated amorphous Si by the disorder model.[16]

We will modify the disorder model of inorganic semiconductors in order to apply it to organic materials with a high rate of geminate recombination. Let us consider an electron-hole pair generated at or just below the mobility edge of an amorphous semiconductor at zero temperature. The pair is generated quite close together because of the exponential decay their overlap integral with distance. In this analysis the fate of one electron-hole pair is described assuming that the electron is fixed in space. The hole can take part in two competing processes: it can hop down in energy because T = 0 K to the nearest localized state of the tail, at distance r, with the rate

$$\nu_d(r) = \nu_0 \exp(-2r/a), \tag{1}$$

or it can recombine with the hole at a rate

$$\nu_r(r) = \tau_0^{-1} \exp(-2R/a), \tag{2}$$

where R is the electron-hole separation and a is the localization radius of the electron. The prefactor ν_0 is the phonon frequency ($\approx 10^{12}$ s^{-1}) and τ_0 is the dipole radiation lifetime ($\approx 3 \times 10^{-11}$ s) which is estimated from the lifetime[17] $\tau \approx 1$ ns of the photoluminescence using the relation[16] of $\tau = \tau_0^2 \nu_0$.

It is clear from Eqs. 1 and 2 that due to inequality $\nu_0 > \tau_0^{-1}$, the probability of diffusion is not negligible for the first steps. After each hop, the average concentration of accessible states decreases and the distances R and r increase. The geminate recombination probability is small when $R < R_c$, where $R_c = (a/2)\ln(\nu_0\tau_0)$ is the characteristic length. It reaches a maximum near $R = R_c$ and then decreases with increasing R. The survival probability of pairs is given by

$$\phi(R) = A(R_c/R)^{\beta}, \tag{3}$$

with A = 3.0, where β = 1.5 is adopted instead of β = 1 used for the inorganic case by taking into account the high geminate-recombination probability. The nongeminate recombination that contributes to the photoconductivity appears when R becomes about half the average carrier separation $0.5n_0^{-1/3}/2$ ($> R_c$) where n_0 is the steady state electron (or hole) concentration under the generation rate G at T = 0 K. Assuming that the band tails have the DOS correspond to an exponential distribution with the width ε_0, we have the expression for the normalized photoconductivity given by

$$\frac{\sigma_p}{eG} = \frac{ea^2}{4\varepsilon_0}\left[\ln(\nu_0\tau_0)\right]^{1.5} L^{0.5}, \tag{4}$$

where $L = n_0^{-1/3}/a$ and is the solution of the equation

$$L = \ln\left\{3G\tau_0 a^3\left[L\ln(\nu_0\tau_0)\right]^{1.5}\right\}^{-1}. \tag{5}$$

Using the experimental value $G = 10^{19}$ $cm^{-3}s^{-1}$, the experimentally determined value ε_0 = 0.04 eV (from Fig. 1) and the reasonable material parameters $\nu_0\tau_0$ = 30 and a = 1 nm for an electron (the value for an electron might be larger than that for a hole, and the larger value would be effective for the recombination), we obtain $\sigma_p/eG = 2 \times 10^{-12}$ cm^2/V for the PMPS from Eq. 4. The estimated value of σ_p/eG is in agreement with the experimental result in Fig. 2. Furthermore, this theory predicts that the temperature T_r where the photoconductivity begins to rise (the transport energy crosses the zero-temperature Fermi level) is $3\varepsilon_0/2kL$, where k is the Boltzmann's constant. The parameters for PMPS give T_r = 30 K. It can be seen in Fig. 2 that the photoconductivity begins to rise around 30 K, however the sharp rise occurs at 100 K and 200 K. The rise at rather high temperatures has been observed for the case of hydrogenated amorphous SiN.[18] This could be related to carrier transport properties such as mobility. The oriented polysilane film that should have higher mobility[2] than the unoriented polysilane film has lower value of T_r.

It has been confirmed that the photocurrent varies in a superlinear fashion with the electric field. This can be explained by the electric field distortion not only of the Coulombic potential field between an electron-hole pair, but also of the potential between nearest hopping sites.

The unusual temperature dependence of dark and photocurrent observed for the C_{60} doped PMPS film is explained as follows. The photogenerated electrons in the polysilane transfer to C_{60} as denoted by (5) in Fig. 4 and holes can stay long in the polysilane because of the spatial separation from electrons. At a low temperature, holes are trapped in the tail states. The accumulation

of the trapped holes shifts their quasi-Fermi level toward, or into, the HOMO band and then the dark and photocurrent become larger and larger with time. The measurement was carried out with increasing temperature so that the variation at 15 K < T < 130 K reflects the accumulation of trapped holes. The pointwise-manner detection of data could not remove the trapped holes in this case. As temperature rises beyond 130 K, the trapped holes in the polysilane and the electrons trapped at the lowest level in the LUMO band of C_{60} are thermally excited to recombine each other, by which the dark current decreases and the ratio of the photocurrent to the dark current becomes large.

We have confirmed that the accumulation of trapped holes does not occur by the excitation using the photon energy of 2.25 eV is difficult, indicating that process 3 in Fig. 4 is not efficient at a low temperature, although it contributes to high photoconduction at room temperature. These results eliminate the possibility[6] of the energy transfer from PMPS to C_{60} followed by process 3 at a low temperature. However, it might be possible at high temperature and could cause the dip of I_d and I_p curves at 160 K. This inference is not conclusive and is subject to further study.

Conclusion

The photoconduction spectrum of PMPS film has an onset 0.1 eV higher than that of the optical absorption. This photoconduction is not caused by free carriers created from excitons at the electrodes. For the free-carrier generation in the bulk, the disorder model is more likely than the charged polaron model. Analysis based on the disorder model has successfully explained the zero-temperature photoconductivity. Doping of C_{60} efficiently sensitizes the photoconduction of PMPS in the spectral region where C_{60} has optical absorption. This sensitization is suppressed at low temperatures. In the low temperature region, photogenerated holes are trapped in the tail states of PMPS in C_{60} doped films. The accumulation of trapped holes moves the Fermi level to increase the dark and photoconductivity. The holes trapped in PMPS and the electrons trapped in C_{60} are thermalized to recombine each other at temperatures higher than 130 K. ◬

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