Thermoelectric transport properties of the n-type impurity Al in PbTe

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Thermoelectric transport properties of the n-type impurity Al in PbTe

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Abstract

Because Tl and In are known to be resonant levels in IV-VI semiconductors, here we synthesize and electrically characterize lead telluride doped n-type with aluminum. The results show that Al behaves as a normal donor in PbTe, reaching a maximum electron concentration of 4 10^{19} cm^{-3}. At 300K, the thermopower, when plotted as function of electron concentration (the Pisarenko relation), follows the calculated line for the conduction band of PbTe, and no enhancement is observed that could indicate the presence of a resonant level.

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In the field of thermoelectricity, one desires to maximize a material's figure of merit $zT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient or thermopower, $\sigma=1/\rho$ the electrical conductivity (ρ=resistivity) and κ the thermal conductivity. After the identification of Tl as a p-type resonant impurity in PbTe that can increase zT,[1] we sought other impurities that could act as n-type resonant levels. This increase in zT is due to an increase in hole effective mass from a distortion in the density of states of the Tl impurity in the valence band. The group III elements, when substituted for Pb as dopants in PbTe, introduce energy levels that increase monotonically in energy with reference to the hydrogen level as their electronegativity (and mass) decreases[2,3]: Tl is in the valence band of PbTe[1]. Indium is in the conduction band at low temperature; due to the increase in the band gap of PbTe, it shifts into the gap at elevated temperature[4]. The case of Ga is more complicated than that of In and Tl, and the existing literature is reviewed in Ref [2]: Ga is a donor that can pin the Fermi energy at one of two possible values. The electron concentration in Ga-doped PbTe can be pinned at either 10^{13} cm^{-3} (at 77K) or in the 10^{18} to 10^{19} cm^{-3} range, depending on the sample preparation method.[2] In the Russian literature, Al is reported by optical measurements to have a level that lies ~300 meV above the conduction band minimum at low T.[5] Since optimum resonant levels for maximizing the thermoelectric performance of semiconductors are known to be based on s-s or s-p interactions between guest specie and host semiconductor electron levels,[6] the purpose of this investigation is to determine if Al acts as a resonant level in PbTe and effectively increases the thermopower and the effective mass.

Ingots of $Pb_{1-x}Al_xTe_1$ with $x\leq0.01$ were synthesized by loading stoichiometric amounts of pure elements of 99.999% purity or greater into carbon coated fused quartz ampoules which were then sealed under a vacuum of at least 10^{-6} torr. The samples were heated to 1000°C, and

subsequently annealed at 800°C. Samples underwent the heat treatment simultaneously to eliminate any variation in sample preparation. X-ray fluorescence measurements were attempted to determine the Al concentration x, but the element is too light to obtain reliable values; only nominal values for x will be used here.

Transport properties were measured on parallelepipeds cut from the ingots (1.5x1.5x6 mm^3) in a liquid nitrogen cooled cryostat from 80-420K and -1.5 to +1.5T. We report here on four transport properties: electrical resistivity (ρ) and Hall coefficient (R_H) were measured using an AC bridge while Seebeck (S) and adiabatic transverse Nernst-Ettingshausen (Nernst or N) coefficients were measured using the static heater and sink method. We measured S with two copper-constantan thermocouples of 0.001" diameter. We measured the temperature difference ΔT with type-T thermocouples comprised of 40μm diameter wires. The diameters of the wires are kept small as possible to minimize heat leakage. The copper leads of the type-T thermocouples also measure the Seebeck voltage, and we estimate the error on this measurement to be 3%. Electrical resistivity was taken using an AC 4-wire bridge measurement, and the error is estimated to be 10%, mainly from inaccuracies in measurement of sample geometry. R_H and N were measured with transverse copper leads, and we estimate the error in these measurements to be 5%. We applied the standard correction[4] to convert from adiabatic to isothermal N and further define R_H and N to be the low field slopes of the Hall resistance and Nernst voltage, respectively.

Galvanomagnetic and thermomagnetic data on materials with 1-1 substitution of Al for Pb are shown in Fig. 1 as a function of temperature at zero magnetic field. We will begin our interpretation of the data with the electron carrier concentration (n), which is calculated from the R_H using $n = r_H / eR_H$ and assuming a Hall prefactor r_H of unity. Because n has only negligibly small temperature dependence, due to the change of the dominant scattering mechanism which

affects the Hall prefactor r_H, we take n at 300K for this discussion. For x=0.125% (or 1.85 x 10^{19} Al atoms per cm^3), the doping efficiency is approximately 2 electrons for 3 Al atoms (inset Fig. 1), which, given the uncertainty on both n and x, is not a significant deviation from unity. This efficiency repeats for x=0.25%, and 0.5%, however, for the x=1% the hole concentration saturates. The surface of the ingot with x=1% became blackened upon cutting in water, presumably from reacting excess unbonded Al , which leads us to believe that the solubility limit of Al in PbTe is between 0.5% and 1%. The very slight increase in ρ in the 1% sample corroborates this hypothesis: additional Al atoms beyond about 0.5% may act as additional scattering centers that limit the mobility. We will therefore limit the majority of our analysis to the three samples with x < 1% Al.

Moving to the other transport properties, the electrical resistivity at 300K monotonically decreases with Al concentration and thus carrier concentration. Electrical mobility (not shown in Fig. 1) deduced from n and ρ at 300K is quite high, 1300 cm^2/Vs for x=0.125%, and dropping to 750 cm^2/Vs for x=0.5%. We see this as initial evidence that the Fermi level is not near a resonant level, as the electrical mobility is a strong function of carrier effective mass and these values are too high for an increase in effective mass over the conduction band of PbTe at 300K.[7] Interestingly, ρ for all samples converges at low temperature to very similar values. S above 200K is approximately linear with temperature, as expected from the metallic resistivity and the Mott relation for degenerate semiconductors. Below 200K, we note nonlinearity in S, which can possibly be ascribed to a change from mostly acoustic phonon scattering at low temperature toward more optical phonon scattering at high T; however this also occurs at the temperatures where ρ converges. The magnitude of S decreases with increasing electron density, as expected for simple band conduction. Furthermore, a line drawn through high temperature slope of S does

not pass through zero at 0K, which probably arises from the previously discussed reasons for the nonlinearity in *S*. Nernst has two distinct temperature dependences, split between low and high amounts of Al impurity and has a similar magnitude to other similarly doped n-type PbTe.[8] In Figure 2, we plot *S* at 300 K as a function of *n*, a plot known as a "Pisarenko relation".[6] This relation can be calculated assuming acoustic phonon scattering and the known conduction band structure of PbTe,[7] and the results are shown as the full line in Fig. 2. The data points for Al-doped samples lie on the calculated line, and the enhancement of *S* customarily observed for resonant levels[6,9] is thus absent here.

Further analysis of the data is possible using the "method of the four coefficients" for degenerate semiconductors.[10] Here, the experimental Seebeck coefficient, electrical resistivity, Nernst–Ettingshausen, and Hall coefficients are related to the following fundamental properties: Fermi energy E_F, carrier mobility, effective mass m^*, and scattering exponent λ. The latter quantity is defined by the energy (E) dependence of the relaxation time $\tau = \tau_0 E^{\lambda - 1/2}$, where $\lambda = 0$ for acoustic phonon scattering, 1 for optical phonon scattering, and 2 for ionized impurity scattering. The results are shown in Fig. 3. In all our samples, the Fermi energy E_F lies well below the 300 meV where optical measurements[5] place the Al level: assuming that Al were a resonant impurity in PbTe with an energy level of 300 meV, one cannot introduce enough electrons by Al-doping to place the Fermi energy at that value. The effective mass in Fig. 3 is if anything a little lighter than the density-of-states band mass in the conduction band of undoped PbTe ($m^* \sim 0.28\ m_e$ at n=2x10^{19}cm^{-3} and $m^* \sim 0.32\ m_e$ at n=4x10^{19}cm^{-3}),[11] the opposite of what is expected for a resonant level. The scattering parameter is indicative that the dominant scattering mechanisms are acoustic and optical phonon scattering, but λ is much lower than expected for resonant[6] scattering or other energy-selective[12] scattering effects.

In summary, we have characterized the behavior of Al in PbTe from 80-420K. Al is a nearly-monovalent donor, whose energy level lies deep in the conduction band and does not increase the thermopower over the Pisarenko relation. If it is a resonant level at all, Al concentrations far above the solubility limit need to be used to place the Fermi level near the Al impurity level. In general, the mobility of Al-doped material is quite good, so that it might prove a practical and simple donor.

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Figure Captions

Figure 1. Thermopower S, resistivity ρ, Nernst-Ettingshausen Coefficient N, and Hall Coefficient R_H of $Pb_{1-x}Al_xTe$. The inset shows the carrier concentration from Hall measurements as a function of nominal Al concentration. Symbols are experimental points; lines are added to guide the eye.

Figure 2. Pisarenko plot for $Pb_{1-x}Al_xTe$. Symbols are experimental points, the solid line is calculated for the lowest conduction band in PbTe.

Figure 3. Results from the 4-parameter fit to the data of Fig. 1. The accuracy of the fits is within $\pm 0.05\ m_e$ for m^*, ± 20 meV for E_F, and ± 0.2 for λ. The results for x= 0.5% and 1% are therefore not significantly different.

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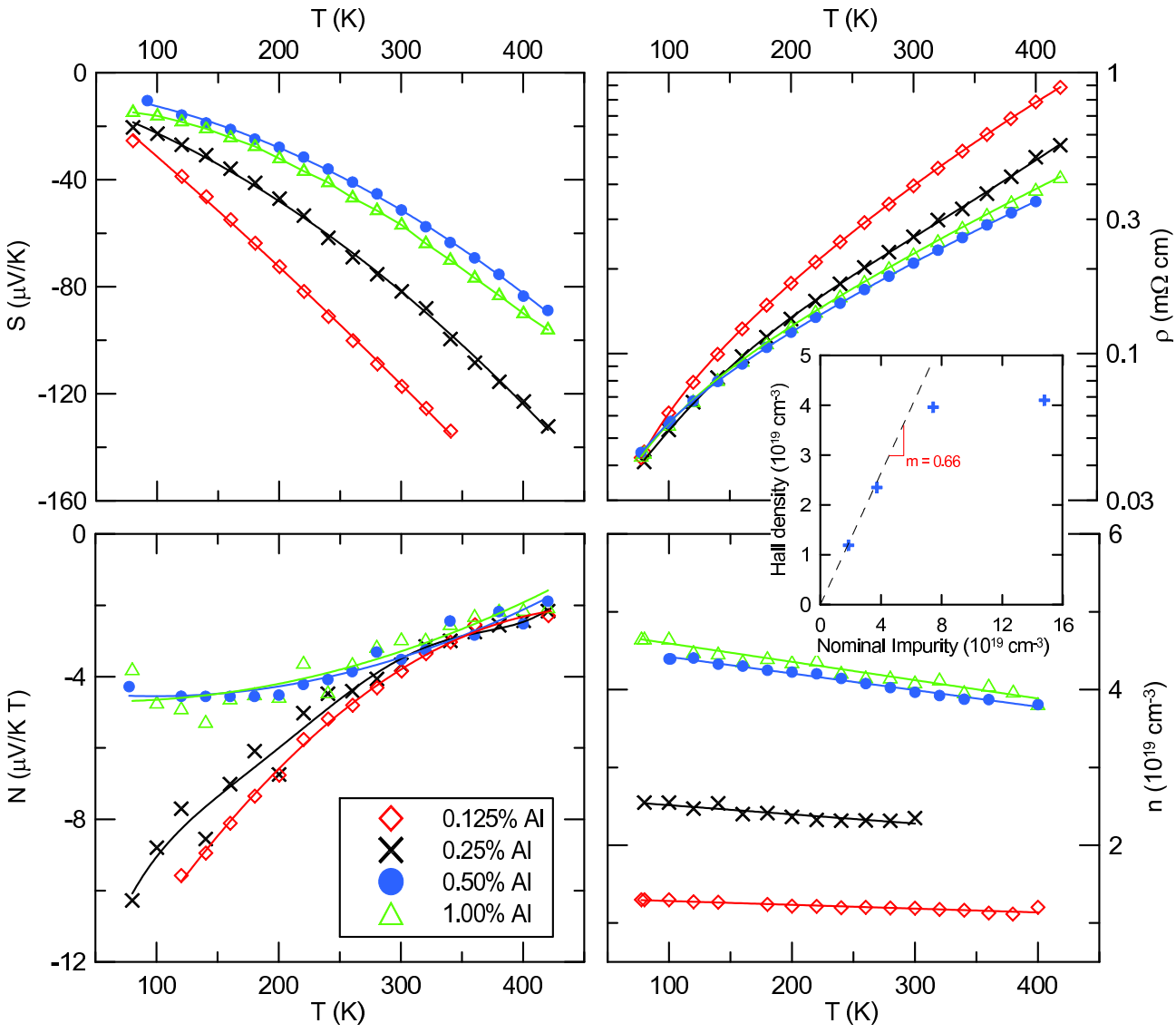

Figure 1 BKJ1161 03JAN2012

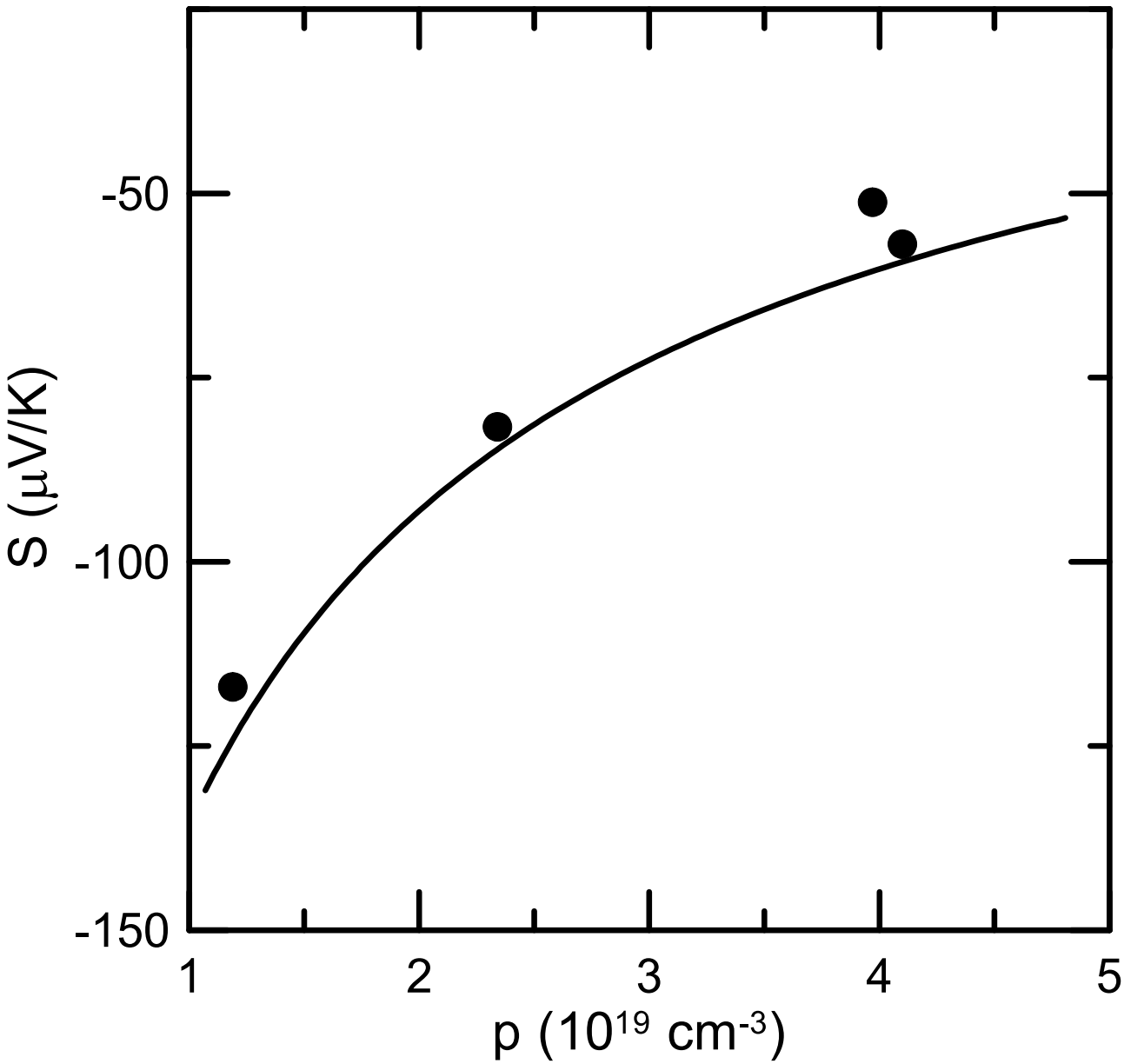

Figure 2 BKJ1161 03JAN2012

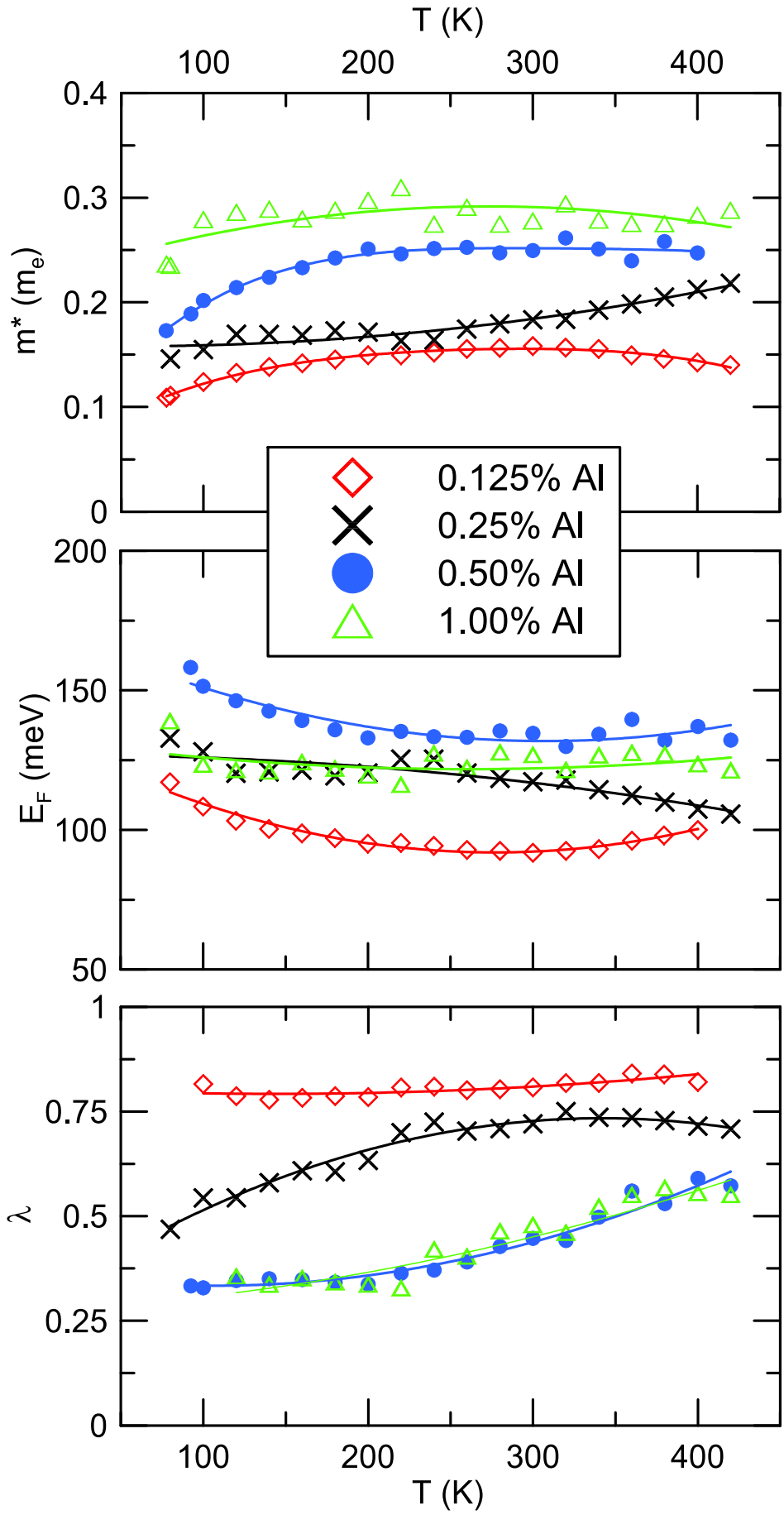

Figure 3 BKJ1161 03JAN2012