J. Phys. B: Atom. Molec. Phys. 13 (1980) 2051–2059. Printed in Great Britain

Oscillator strengths of Ti II from combined hook and emission measurements

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Received 19 November 1979, in final form 7 January 1980

Abstract. It is demonstrated that a large set of accurate oscillator strengths of Ti II can be determined from a combination of hook and emission measurements without any assumption concerning the plasma state. Modified cascaded arcs and hollow cathode discharges have been used as plasma light sources for both hook and emission measurements. The relative f values have been converted to an absolute scale by means of literature data. The overall uncertainties of the f values are about 13–25%. Comparisons with other experimental and theoretical data are made which indicate excellent to fair agreement. Only for one of the published data sets has a wavelength-dependent discrepancy of up to a factor of two been found.

1. Introduction

A very reliable method with which to obtain large sets of accurate oscillator strengths is that based upon a combination of emission measurements of lines having a common upper level with hook or absorption measurements of lines having a common lower level. Obviously, if separate sets of f values have one line in common they may be linked together (see e.g. Ladenburg 1933, Pery-Thorne and Chamberlain 1963, Kühne *et al* 1978). The procedure is shown schematically in figure 1. The figures 1(a) and 1(b) are examples of transitions which pertain to a common lower and upper level, respectively; the transition $0 \leftrightarrow m$ is shared by both sets. An extension of the procedure to excited levels that may be called 'leap frogging' (see Huber 1977) is shown in 1(c): the transition $n \leftrightarrow j$, measured in emission (E), may be linked to the transition $0 \leftrightarrow 1$, measured by absorption or by the hook technique (H).

There are two difficulties in applying this procedure.

(i) Under the assumption that all measurements have about the same statistical error the uncertainty of a relative f value that has been linked in n stages will be increased by a factor of $\sqrt{n}$.

(ii) Light sources are required that generate sufficient population of excited levels and if possible in different stages of ionisation for both emission and absorption (hook) measurements. Otherwise it is no longer possible to create extensive sets of f values according to figure 1(c), including resonance lines as well as lines from highly excited levels.

There are also outstanding advantages.

(i) It is not necessary to know the plasma state, i.e. the LTE assumption and temperature measurement are avoided thus reducing the number of sources of possible systematic errors.

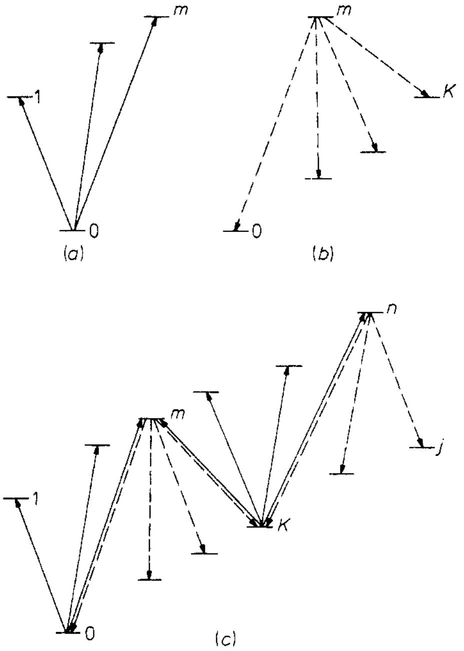

Figure 1. Schematic representation of combining hook and emission measurements. In (*c*) $f^{E}_{nj}/f^{H}_{10} = (f^{E}_{nj}/f^{E}_{nk})(f^{H}_{nk}/f^{H}_{mK})(f^{E}_{mK}/f^{E}_{m0})(f^{H}_{m0}/f^{H}_{10})$.

(ii) Different, specifically designed, light sources may be used for hook and emission measurements.

(iii) The possibility of linking a line in several different ways reduces the risk of systematic errors as shown in figure 2 and reduces the statistical errors: if a line in the nth stage of the linking may be linked in m different ways, the statistical error will only be enhanced by a factor $\sqrt{n/m}$.

We have tested the method by measuring a large set of Ti I oscillator strengths (Kühne *et al* 1978).

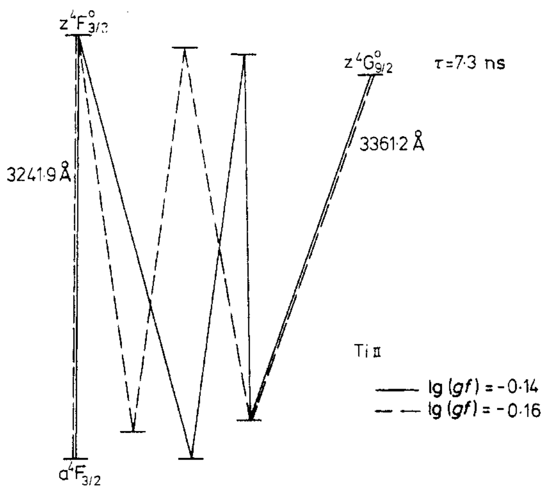

Figure 2. Example for two possible linkages of the lines 3241·9 Å and 3361·2 Å.

For the first time, in this paper we shall fully utilise the advantages mentioned to obtain a reliable set of Ti II f values from combined hook and emission measurements on different light sources.

2. Light sources

We have employed three types of light sources for this investigation: a quartz tube arc, a cascaded arc and a hollow cathode discharge. All three types of plasma light source are designed for both hook and emission measurements. Thus it was possible to test that the measurements are independent of the plasma state. One result of our investigation therefore will be that a non-thermal hollow cathode discharge can be used for elements which are extremely difficult to handle in arcs.

The hook measurements have primarily been performed with a specially designed wall-stabilised arc (see Kock and Kühne 1977), whose centre section consists of a double-walled, air-cooled quartz tube of 16 mm diameter and 120 mm length. The arc has been operated with argon as a carrier gas at atmospheric pressure and at a current of 25 A. The inner quartz wall attains a temperature of about 1000 °C during operation. By passing carefully dried argon over a surface of liquid $TiCl_4$ which could be kept at a fixed temperature between 20 °C and 150 °C a fixed proportion of titanium was continuously fed into the centre section of the arc.

One part of the emission measurements has been performed with a cascaded three-chamber arc especially designed to excite metallic components (Kühne *et al* 1978). The technique is well known and is described, e.g., by Bell *et al* (1965), Kock and Richter (1968), Bridges and Wiese (1970). The arc has a bore of 16 mm diameter and a length of 120 mm. The arc has been operated in argon at atmospheric pressure and at a current of 25 A. The continuous mixing of argon and $TiCl_4$ was achieved in the same way as described above.

Another light source used for the emission measurements is a hollow cathode discharge (see e.g. Elander and Neuhaus 1974). The construction is shown schematically in figure 3. It consists of two anodes to achieve a symmetrical discharge and one cathode which contains an exchangeable cylindrical titanium plug with a straight-through bore of 8 mm diameter and a length of 100 mm. The electrical insulation of the water-cooled electrodes is performed by glass tubes. All parts are vacuum sealed. The construction of the tube is designed to allow hook measurements as well.

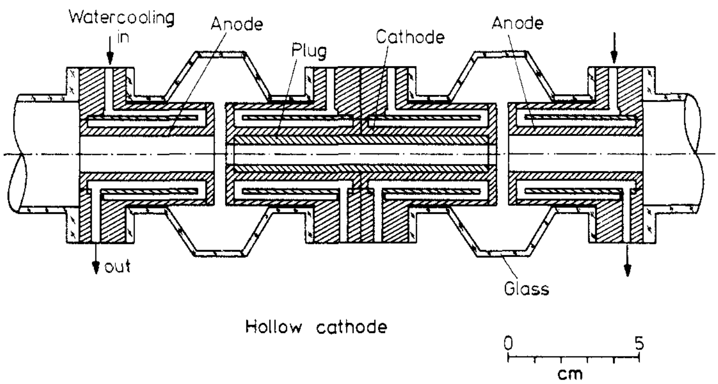

Figure 3. Longitudinal section of the hollow cathode.

We have operated the discharge at currents between a few mA (for emission measurements) and 20 A (for hook measurements). The maximum current was only limited by the power supply. Optimum burning conditions have been achieved for titanium with neon as a buffer gas at a pressure of 7 mbar. From hook measurements we found for both Ti I and Ti II a number density of 10^{14} cm^{-3} at a discharge current of 20 A. The interferometric quality of the plasma column is remarkably good.

3. Experimental

The set-up of our hook experiment was similar to that described in an earlier paper by Kock and Kühne (1977). It consisted of the quartz-tube arc, a high-power capillary discharge as a continuum light source, a Michelson interferometer with quartz optics and a stigmatic spectrograph.

The spectrograph is a 3·4 m Ebert configuration with a plane grating of 1200 lines mm^{-1} producing a reciprocal linear dispersion of 2·4 Å mm^{-1} in the first order.

A 25 μm wide and 3 mm high slit was used throughout. The spectra were photographed on Ilford FP4 film. The hook spectra were evaluated by means of a high-precision comparator connected to a computer. Following the suggestion of H A Bachor (1979 private communication) only hooks with a separation of at least 300 mÅ have been evaluated.

The emission measurements have been performed photoelectrically using a photon counting system and a 2 m McPherson monochromator with plane gratings of 1200 and 2400 lines mm^{-1} respectively. The line intensities have been calibrated with a carbon arc as a radiation standard using the absolute data given by Einfeld and Stuck (1978) and Magdeburg and Schley (1966).

Since the scope of measurements has been reduced to relative intensities of lines from the same upper level, self absorption is the only possible source of systematic errors for the line intensities. Self reversal of the resonance lines can be excluded for ionised titanium. Nevertheless we have checked that these lines are free from self reversal in our three-chamber arc where the cold boundary layers are free from the metal component.

Self absorption of the lines has been checked in two different ways. Firstly, by placing a carefully aligned mirror at the distance of its curvature radius behind the hollow cathode the intensity of an optically thin line with the mirror (I_M) will be

$$I_M = I(1+\epsilon_\lambda)$$

if I is the intensity without the mirror and ϵ_λ the reflectivity of the mirror times the transmission of the windows at wavelength λ. The value ϵ_λ had been determined separately. In addition, the line intensity ratio of strong and weak lines originating from the same upper level has been observed during variation of the discharge current. If the strongest line tends to become optically thick, this ratio will change.

For currents smaller than 100 mA most of the lines were found to be free from self absorption to within the experimental errors.

For the arc measurements the lines of interest were checked by estimating the maximum optical thickness in the following manner. The integrated intensity of a Gaussian profiled line is expressed by

$$I_L = I_{\lambda,\max}\sqrt{\pi}\,\Delta\lambda_D$$

where $I_{\lambda,\max}$ is the maximum intensity at the line centre and $\Delta\lambda_D$ the 1/e halfwidth of the line. If the lines are broadened at least by the thermal Doppler effect an estimate of the maximum optical thickness is given by

$$\tau_{\max} \leq I_L / (\sqrt{\pi}\, \Delta\lambda_D\, B)$$

where B is the Kirchhoff–Planck function. Since only lines with a $\tau_{\max} < 0{\cdot}1$ have been evaluated no corrections to optically thin layers were necessary. For the calculation of $\Delta\lambda_D$ a rough temperature determination was carried out from Ar and Ti line intensities yielding temperatures of about 8000 K in the arc axis.

4. Results and discussion

In the first step thirty-two lines arising from eight different lower levels could be hooked giving eight independent small sets of relative f values. These lines reach thirteen different upper levels, so that in the second step we determined thirteen sets of relative f values by emission measurements. The principle of linking together these separate sets is shown in figure 1(c). By this method we obtained a total set of relative oscillator strengths comprising sixty seven lines, which still had to be normalised to absolute values.

Roberts *et al* (1973) have measured lifetimes of Ti II levels by the beam–foil technique. The quoted errors are smaller than ±10% for levels which are not affected by cascade corrections. If one knows the lifetime of an excited level and the branching ratios of all transitions from this level it is possible to convert these values into absolute oscillator strengths. We have chosen the level $z^4G^o_{9/2}$ ($\tau = 7{\cdot}3$ ns) for

(i) the number of transitions from this level is small and dominated by one strong line,

(ii) none of the lines from this level is affected by blends, and

(iii) the lifetime needs no cascade correction.

The complete set of absolute f values is listed in table 1. The quoted errors are composed of the statistical uncertainty of the emission measurements as well as the hook measurements (standard deviation of the mean, evaluated from five and ten independent runs, respectively) and the error of the lifetime used. The errors are obviously dependent on the number of necessary links (up to five).

Because of the great complexity of the spectrum in most of the cases there are several ways to proceed from one line to another (see figure 2). By checking the outcomes of all the possible ways of obtaining an f value for a given line it is possible to eliminate eventual systematic errors and to reduce the limits of uncertainty.

Moreover a consistency check can be carried out in the manner described below. If four or more sets which alternately have common upper and lower levels are considered, and if any two consecutive sets have one line in common, then it may be possible to form a loop of linkings such that the final transition coincides with the starting transition, whose lg gf value has been arbitrarily put to zero. In this way the relative lg gf values of all lines under consideration should add up to zero (in a sense the procedure reminds one of the voltage mesh rule of an electric network). An example for a closed loop may be seen in figure 2 if one combines the full with the broken paths. By this method single measurements which are grossly in error will be excluded. Both of these tests gave deviations which were smaller than the limits of quoted error.

Table 1. Absolute oscillator strengths for Ti II.

Wavelength (Å)	Multipet No	Transition	lg (*gf*)	Error (%)
3066·22	5	$a^4F_{5/2}-z^4D^o_{5/2}$	−0·72	20
3066·35	5	$a^4F_{3/2}-z^4D^o_{3/2}$	−0·73	20
3072·11	5	$a^4F_{7/2}-z^4D^o_{7/2}$	−0·66	16
3072·97	5	$a^4F_{3/2}-z^4D^o_{1/2}$	−0·38	19
3075·22	5	$a^4F_{5/2}-z^4D^o_{3/2}$	−0·15	16
3078·64	5	$a^4F_{7/2}-z^4D^o_{5/2}$	−0·04	15
3088·03	5	$a^4F_{9/2}-z^4D^o_{7/2}$	+0·20	15
3152·25	10	$b^4F_{5/2}-z^4D^o_{5/2}$	−1·09	18
3154·19	10	$b^4F_{3/2}-z^4D^o_{3/2}$	−1·18	19
3155·67	10	$b^4F_{7/2}-z^4D^o_{7/2}$	−1·05	16
3161·20	10	$b^4F_{3/2}-z^4D^o_{1/2}$	−0·79	20
3161·75	10	$b^4F_{5/2}-z^4D^o_{3/2}$	−0·57	18
3162·57	10	$b^4F_{7/2}-z^4D^o_{5/2}$	−0·46	16
3214·75	3	$a^4F_{9/2}-z^2F^o_{7/2}$	−1·42	16
3217·06	2	$a^4F_{7/2}-z^4F^o_{9/2}$	−0·55	16
3222·84	2	$a^4F_{5/2}-z^4F^o_{7/2}$	−0·48	17
3226·77	3	$a^4F_{7/2}-z^2F^o_{5/2}$	−1·88	18
3234·52	2	$a^4F_{9/2}-z^4F^o_{9/2}$	+0·31	15
3236·57	2	$a^4F_{7/2}-z^4F^o_{7/2}$	+0·12	15
3239·04	2	$a^4F_{5/2}-z^4F^o_{5/2}$	0·00	15
3241·98	2	$a^4F_{3/2}-z^4F^o_{3/2}$	−0·15	18
3251·91	2	$a^4F_{5/2}-z^4F^o_{3/2}$	−0·64	16
3252·91	2	$a^4F_{7/2}-z^4F^o_{5/2}$	−0·45	20
3254·26	2	$a^4F_{9/2}-z^4F^0_{7/2}$	−0·59	16
3308·84	7	$b^4F_{7/2}-z^4F^o_{9/2}$	−1·13	19
3318·06	7	$b^4F_{5/2}-z^4F^o_{7/2}$	−1·10	16
3322·94	7	$b^4F_{9/2}-z^4F^o_{9/2}$	−0·12	19
3326·76	7	$b^4F_{3/2}-z^4F^o_{5/2}$	−1·07	15
3329·45	7	$b^4F_{7/2}-z^4F^o_{7/2}$	−0·35	15
3335·19	7	$b^4F_{5/2}-z^4F^o_{5/2}$	−0·46	16
3340·34	7	$b^4F_{3/2}-z^4F^o_{3/2}$	−0·63	16
3343·77	7	$b^4F_{9/2}-z^4F^o_{7/2}$	−1·27	18
3346·72	7	$b^4F_{7/2}-z^4F^0_{5/2}$	−1·08	15
3361·21	1	$a^4F_{7/2}-z^4G^o_{9/2}$	+0·28	13
3372·80	1	$a^4F_{5/2}-z^4G^o_{7/2}$	+0·18	15
3380·28	1	$a^4F_{9/2}-z^4G^o_{9/2}$	−0·58	13
3383·76	1	$a^4F_{3/2}-z^4G^o_{5/2}$	+0·09	19
3387·83	1	$a^4F_{7/2}-z^4G^o_{7/2}$	−0·51	15
3394·57	1	$a^4F_{5/2}-z^4G^o_{5/2}$	−0·57	16
3407·21	1	$a^4F_{9/2}-z^4G^o_{7/2}$	−2·05	19
3409·81	1	$a^4F_{7/2}-z^4G^o_{5/2}$	−1·90	16
3461·50	6	$b^4F_{7/2}-z^4G^o_{9/2}$	−0·87	13
3477·18	6	$b^4F_{5/2}-z^4G^o_{7/2}$	−1·09	19
3491·05	6	$b^4F_{3/2}-z^4G^o_{5/2}$	−1·07	15
3596·05	15	$a^2F_{7/2}-z^4D^o_{5/2}$	−1·22	16
3721·63	13	$a^2F_{5/2}-z^2F^o_{7/2}$	−1·19	18
3759·29	13	$a^2F_{7/2}-z^2F^o_{7/2}$	+0·20	18
3761·32	13	$a^2F_{5/2}-z^2F^o_{5/2}$	+0·10	18
3987·63	11	$a^2F_{7/2}-z^4G^o_{9/2}$	−2·73	18
4012·37	11	$a^2F_{5/2}-z^4G^o_{5/2}$	−1·61	16
4301·93	41	$a^4P_{1/2}-z^4D^o_{3/2}$	−1·16	17
4312·86	41	$a^4P_{5/2}-z^4D^o_{5/2}$	−1·16	19
4314·98	41	$a^4P_{1/2}-z^4D^o_{1/2}$	−1·13	19
4320·97	41	$a^4P_{3/2}-z^4D^o_{1/2}$	−1·87	19

Table 1. (continued)

Wavelength (Å)	Multiplet No	Transition	lg (*gf*)	Error (%)
4330·71	41	$a^4P_{5/2}$–$z^4D^o_{3/2}$	−2·04	19
4394·06	51	$a^2P_{1/2}$–$z^4D^o_{3/2}$	−1·59	25
4399·77	51	$a^2P_{3/2}$–$z^4D^o_{5/2}$	−1·27	22
4407·68	51	$a^2P_{1/2}$–$z^4D^o_{1/2}$	−2·47	20
4443·80	19	$a^2D_{3/2}$–$z^2F^o_{5/2}$	−0·70	19
4444·56	31	$a^2G_{7/2}$–$z^2F^o_{7/2}$	−2·20	25
4450·49	19	$a^2D_{5/2}$–$z^2F^o_{5/2}$	−1·45	19
4468·49	31	$a^2G_{9/2}$–$z^2F^o_{7/2}$	−0·60	21
4501·27	31	$a^2G_{7/2}$–$z^2F^o_{5/2}$	−0·75	19
4583·44	39	$a^4P_{3/2}$–$z^2F^o_{5/2}$	−2·77	21
4708·66	49	$a^2P_{3/2}$–$z^2F^o_{5/2}$	−2·30	25
5336·81	69	$b^2D_{5/2}$–$z^2F^o_{7/2}$	−1·70	21
5418·76	69	$b^2D_{5/2}$–$z^2F^o_{5/2}$	−1·86	25

Roberts *et al* (1975) performed an arc experiment under LTE conditions to obtain oscillator strengths for Ti I, Ti II and Ti III. As figure 4 shows, there is excellent agreement with our data, the statistical spread being smaller than 9%. No systematic deviation can be discovered, indicating that their LTE assumption and temperature measurement were correct. This result corroborates the method of LTE measurement on a wall-stabilised arc, if it is carried out very carefully.

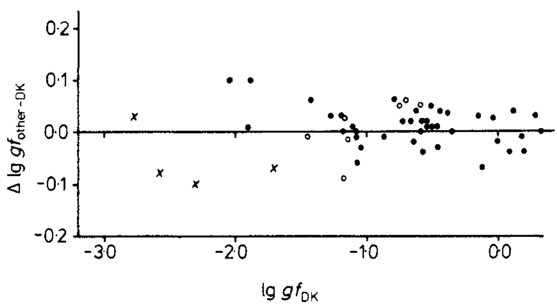

Figure 4. A comparison of lg *gf* values measured by other authors with our data (DK). ●, Roberts *et al* (1975); ○, Wobig (1962); ×, Wolnik and Berthel (1973).

In their paper Roberts *et al* (1975) gave correction factors for the very extensive earlier data of Roberts *et al* (1973) obtained by branching ratio measurements on a flow-stabilised arc normalised by lifetimes from beam–foil experiments.

The comparison in figure 5 shows a strong wavelength-dependent deviation. When we discovered this discrepancy, we carefully checked our results obtained with the hollow cathode. We controlled the stray light, the optical set-up and the carbon arc data. We further repeated parts of the measurements with a wall-stabilised arc as a light source instead of the hollow cathode. All these tests confirm our previous results. Thus we conclude that the data of Roberts *et al* (1973) are incorrect for longer wavelengths. Although we have not discovered the source of their errors, a possible cause may be an incorrect absolute calibration of the intensity over a wide spectral range from the visible to the ultraviolet.

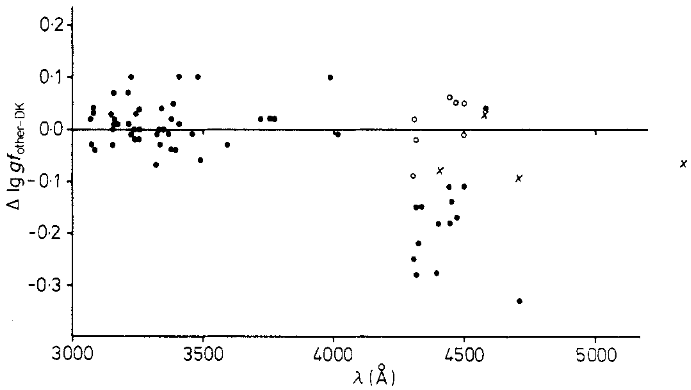

Figure 5. A comparison of lg gf values measured by other authors with our data (DK). The abscissa is the wavelength. ●, Roberts *et al* (1973); ○, Wobig (1962); ×, Wolnik and Berthel (1973).

We have not so many lines in common with Wolnik and Berthel (1973), who obtained their data by emission spectroscopy on a shock tube and Wobig (1962), who performed an arc experiment.

The comparison is given in figures 4 and 5. The scatter is fairly good and no systematic tendency is visible.

Kurucz and Peytremann (1975) have provided a very comprehensive list of calculated f values, most of them being based upon scaled Thomas–Fermi–Dirac radial wavefunctions. As figure 6 shows, the scatter is remarkably small for Ti II compared with similar plots of these data with other elements (Huber and Sandeman 1977, Smith and Kühne 1978, Gehlsen *et al* 1978). No wavelength-dependent deviation can be found.

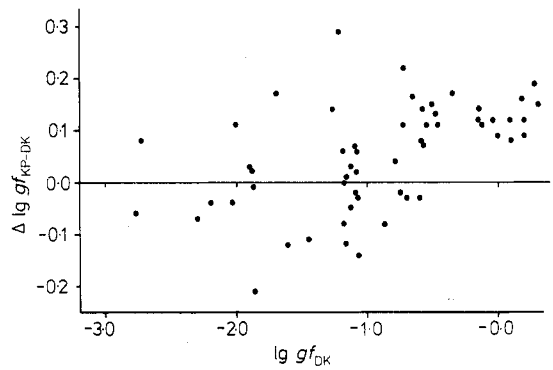

Figure 6. A comparison of lg gf values calculated by Kurucz and Peytreman (1975) (KP) with our data (DK).

5. Conclusion

In conclusion it can be stated that the method of combined hook and emission measurements is well suited to the determination of relative transition probabilities. For the present method neither the assumption of an LTE plasma nor temperature measurements are required, and therefore a great variety of spectroscopic light sources may be used. Both the linking of lines in different ways in complex spectra and the consistency check by closed loops add to the confidence in the reliability and accuracy of the whole set of f values.

Acknowledgment

We gratefully acknowledge fruitful discussions with E Schulz-Gulde.

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