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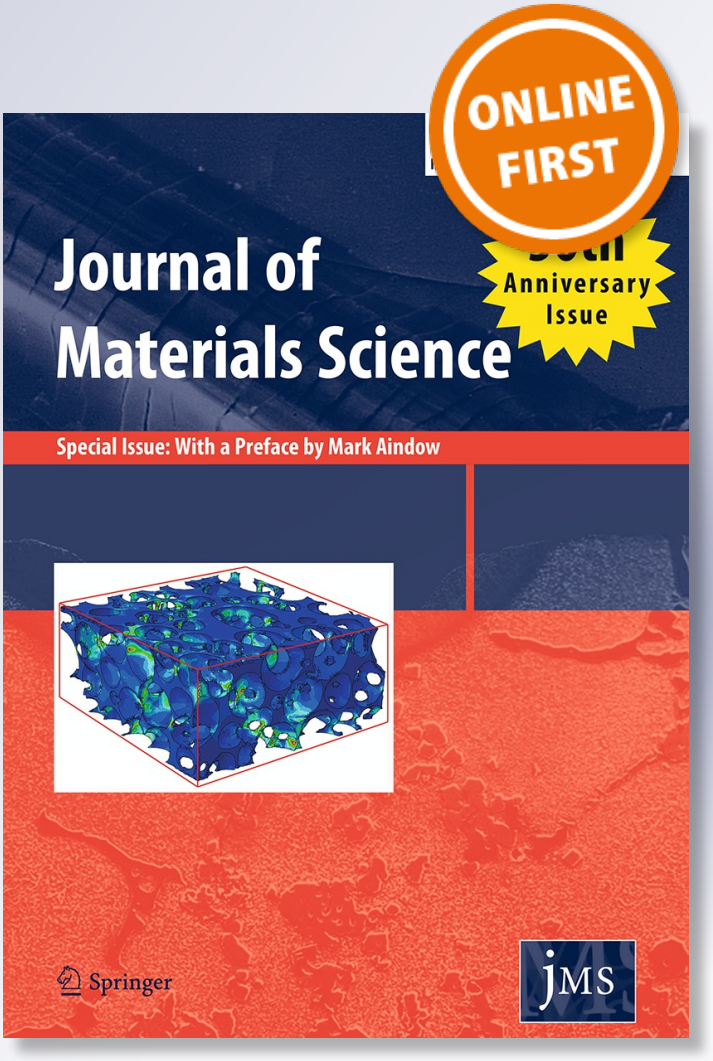

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INVITED VIEWPOINT

On the pressing need to address beam–sample interactions in atomic resolution electron microscopy

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Undeniably, the characterization of solids at the atomic scale using electron beams has become a core aspect of materials sciences. In fact, current abilities of advanced electron microscopes read like a fairy tale: Why not visualize the atomic structure of nanocrystals, defects, and surfaces? No problem, it can be done at a single atom level except for the detection of hydrogen atoms. Are you interested in the chemical composition of nanomaterials at the atomic scale? Atomically resolved maps of elemental distributions can be acquired before lunch, but it takes a little longer if you want to have them in three dimensions. Interested in property–function relationships? In situ microscopy will provide the needed solutions. In any case, "seeing is believing," and one can trust the recorded images of atomic structures since they provide an artifact-free view of nature's secrets and largely make obsolete the old-fashioned art of acquiring and interpreting low magnification images that often exhibit complex diffraction contrast. Certainly, advertisements for electron microscopes read like such tales, but reality must surely be different. Not at all! It is mind-buckling that the reality of forefront electron microscopy nowadays resides in the vicinity of such dream-like capabilities because recent technological advancements have placed electron microscopy into this spot. Never before in its distinguished history was the prospect for further improvements so rich. In fact, its impact reaches beyond materials sciences and rapidly finds applications in the biological and chemical communities such that electron microscopy becomes an outstanding, interdisciplinary research tool. However, such unprecedented progress comes with a price tag that relates to beam–sample interactions. Surely, some remarks are appropriate that lay out why this is the case.

Fig. 1 shows one way of summarizing the accomplishments of electron microscopy in material sciences over the last decade. The viewgraph puts into perspective the resolution improvements of phase-contrast electron microscopy that were achieved in DOE's TEAM Project [1, 2] by optimizing electron-optical components including aberration correctors, monochromators, and high-brightness electron emitters. From the outside, many of the complex instruments look alike but a rich technological diversity that sets their performance is hidden behind cover panels. For example, in the phase-contrast broad-beam mode it is now established that focus spread and image spread limit the achievable resolution [3]. Together they describe a resolution limiting image blur that occurs in direction of the impinging electron beam and in the perpendicular image plane, respectively. In Fig. 1 the TEAM 0.5 microscope is used as a reference point and compared with resolution predictions since it performs at the leading edge of less than 50 pm of resolution since 8 years in focused [1] and broad-beam [2] modes. Technologically, its extraordinary performance is achieved by combining an ultra-twin lens with a short, spherical (Cs)-aberration corrector and exploiting a monochromator using a Nelsonian illumination scheme [4] such that an image spread of only 10–15 pm is present.

It is instructive comparing other physical processes with this magnitude of the image spread in Fig. 1 because it highlights how exceptional the performance of electron microscopes has become. For example, intrinsic vibrations of commercially available side entry holders are around 10 pm. They are also comparable with typical Debye–

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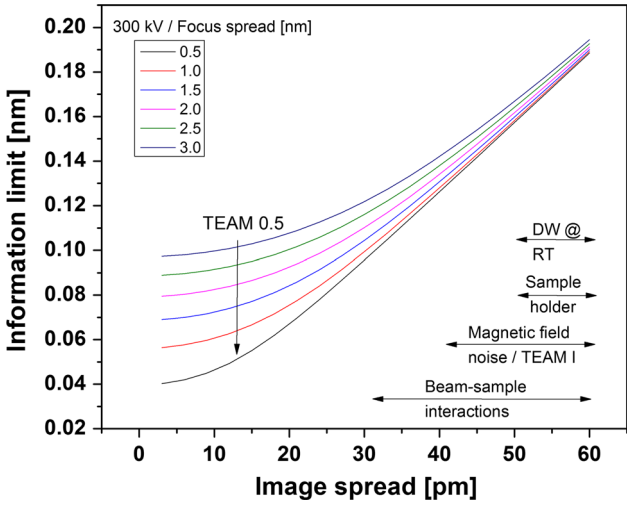

Fig. 1 Calculated dependence of the information limit resolution on image spread and focus spread in phase-contrast electron microscopy [3]. Unavoidable sources of additional image blur between 10 and 30 pm are given by the widths of the plotted arrows. For example, it is seen that the 10–15-pm image spread of the TEAM 0.5 microscope is well comparable with vibrational contributions from sample holders or Debye–Waller factors (DW). Beam–sample interactions are the most prominent source for additional image blur. For more details see text

Waller factors of 0.5–1 Å^2 that describe atom vibrations around their equilibrium position close to room temperature and translate into mean atom displacements [5] of 8–11 pm. The manufacturing of more complex aberration correctors such as a combination of spherical (Cs)- and chromatic (Cc)-aberration corrector doubles the physical length of this optoelectronic element compared with a simpler Cs corrector. As a result, the integrated thermal magnetic field noise along the extended path of the electrons in a column increases the image spread to 15–25 pm [6]. However, it is most remarkable that during the observation of materials at atomic resolution, the electron beam itself induces atom displacements that can reach 30 pm and dominate all other atom displacements long before permanent damage is inflicted to a sample [7]. Typically, such beam-induced, reversible object excitations exceed the intrinsic image spread by a factor of 2–3 if atomic resolution imaging of nanomaterials, surfaces, or molecules is practiced using an established image-acquisition procedure with electron doses between 1000 and 100,000 e/Å^2. It is mandatory to deliver electrons in such large numbers since enough scattering events must occur to ensure that single atoms or atom columns become visible in high-resolution images. Technology allows to drastically vary the rate at which these electrons are delivered so that dose rates as low as 10 e/Å^2 s are used for low dose rate in-line holography [7] and typically reach 1,000,000,000 e/Å^2 s for the acquisition of atomic resolution dark field images using a focused probe. Dose fractionalization takes advantage of this wide range of doses and rates of choice.

Thus, DOE's TEAM project helped us promote a new generation of advanced electron microscopes that now operate close to the fundamental limit of thermally induced atom motion at room temperature! Further progress is possible but challenging. In the first place, it calls not only for a better control of beam–sample interactions [8] but also for a more flexible design of electron-optical components and for a refinement of temperature control if electron beam-induced atom vibrations can be reduced to less than 10 pm. Naturally, these considerations are independent of broad-beam or focused-probe detection modes.

Beam-induced object alterations are not intrinsic to the choice of electron beams for sample illumination. Any probing radiation will cause damage if the deposited energy exceeds threshold values. In this respect, a comparison of electron and X-ray beams is vividly debated in the context of structural imaging of biological objects [9, 10]. Central to such debates is the fundamentally different interaction of electrons and X-rays with matter. Electron scattering is dominated by Coulomb scattering at the nuclei of atoms contributing with elastic scattering events to the image-formation processes, while X-rays are dominantly scattered by the electron cloud surrounding atoms in an inelastic manner, which is why they damage samples more effectively [11]. It was a logic extension for X-ray applications to steadily increase the source brightness such that it became feasible to skillfully exploit "diffract-and-destroy" type of experiments where damage is intentionally inflicted by X-ray bursts but outrun by recording diffraction patterns [10], and excellent spectroscopy is provided. Evidently, the development of electron microscopy on basis of a similar concept would be a less-effective path forward because of the less-damaging nature of their interaction with matter. Nevertheless, such an approach to advance electron microscopy is sometimes debated [12].

On the other hand, it was recently pointed out that dose fractionalization bears significant advantages for the imaging of radiation-sensitive material with electrons at atomic resolution. Related "divide-and-conquer" approaches are currently emerging [7, 13, 14]. They already allow maintaining the pristine structure of catalytic nanocrystals and even molecules [15, 16] because dose fractionalization retards electron beam-induced sample degradation to an unexplored end. In fact, pioneering investigations using low dose rate in-line holography open the exciting perspective that such experiments cannot only be applied in vacuum at room temperature but also at variable temperatures and elevated pressures [15].

Thus, the fundamentally different interaction of electrons and X-rays with matter allows truly complementary approaches to be deployed that target the determination of

structure, composition, and function at the atomic scale, even if radiation-sensitive materials are probed in three dimensions [17]. Certainly, dose fractionalization [8] complements a recent report on future trends in electron microscopy [18] and never before in the history of electron microscopy were the perspectives for technological advancements similarly rich. Strikingly, the day-to-day research with electron beams tells a very different story.

The market for electron microscopes in materials science has boomed during the last decade and continues to grow rapidly in the biological sciences. However, only a few of the wide-spread latest-generation electron microscopes operate at the level of the TEAM 0.5 instrument or similar equipment. Even if available, such instruments are often operated below their optoelectronic limit since it is not unusual that the difference between the information limit of 0.5 Å and a point-to-point resolution around 1.5 Å in Fig. 1 is ignored, and the equipment is used like a more conventional instrument for a variety of other purposes. Materials research can certainly remain outstanding without fully taking advantage of the full sub-Ångstrom resolution, which even complicates matters significantly since beam-induced sample degradation increases rapidly proportional to the square of the magnification. Moreover, in situ electron microscopy has become a main stream activity that appears to perform best at a similarly lower resolution, where a rich variety of in-situ sample holders performs best. Thus, the field seems set to address the "Transformative Opportunities in a New Era of Science" [19] which, however, are mostly defined by vivid contributions from X-ray and biological sciences [9, 10, 19]. So, how is it that the contributions of electron microscopy to this new era of science are not quite as visible as one would expect?

Obviously, there cannot be a unique answer to this question but it is reasonable to address partial aspects by briefly looking at successes and practices of electron microscopy in materials sciences. Scientific highlights certainly include clarifying the internal structure of solids with outstanding research on dislocations and buried interfaces in heterogeneous systems. In case of bulk samples, a deteriorating effect of beam–sample interactions is less critical because acceleration voltages can be chosen well below threshold values for atom displacements [20]. Necessarily, these bulk threshold values systematically exceed equivalent thresholds for atom displacements in surface proximity or at defects [20] because binding energies are reduced and can vary greatly. Thus, any hard onset of damage in the bulk is greatly overwritten by a soft onset of atom displacements in surface proximity for typical electron acceleration voltages between 50 and 300 kV. However, the presence of atom loss in surface proximity easily escapes observations since contributions from a few surface layers to contrast in high-resolution images can rarely be distinguished from the overwhelming bulk contributions [4, 7]. In addition, atom diffusion across surfaces is fast compared with typical image exposure times between 0.1 and 10 s [21] such that any structure appears static even if it is continuously altered in surface proximity during the image-acquisition process. Making things worse, "seeing is believing" is certainly an effective slogan for an advertisement, but it is an entirely inappropriate excuse for any lack of quantitative image interpretations. Scientific methods call for appropriate measurements and not for opinions on visibility. These hidden aspects make the interpretation of image contrast by visual inspection still a common practice, in particular, if it comes to an evaluation of electron beam-induced sample alterations; and adequate choices of low electron doses or dose rates for the image-acquisition processes [7] are commonly treated as if they were a commodity but not a necessity. Consequently, electron beam-induced sample alterations are conveniently ignored by a majority of materials scientists. This unfortunate practice puts many ongoing experiments into a self-consistent comfort zone where spectacular achievements can be reported by simply claiming an absence of beam-induced atom loss even if it is massively present [e.g., 22]. On the other hand, instrumental progress is only pursued gradually. The introduction of advanced camera systems or the collection of large data-sets, for example, currently drive such timely and incremental progress. Moreover, it has also become customary to operate electron microscopes closely following instructions provided by manufacturers. In this process, the complex instruments are treated as black boxes that deliver spectra and images from the atomic structure of matter with an "indisputable and ultimate" performance and little need for accountability. Since material characterization can be perfected iteratively in this manner, it even feels wasteful to spend time on either looking backward at previously established capabilities or forward at a possible evolution of the tool.

A look back in time can appear blurred since many achievements from the past seem forgotten or are replaced by the misleading notion that only the current generation electron microscopes provides state-of-the-art results. For example, it has become common practice to investigate dislocations in high-resolution modes even though diffraction contrast at lower magnification can provide more useful information and damage is greatly reduced. Suitable weak-beam methods are rarely practiced or are no longer known! Similarly, a simple fabrication of an electron transparent cross-sectional sample often becomes an unsurmountable obstacle if an automated Focused Ion Beam procedure is unavailable. Rightfully, expertise and training of the present generation scientists are geared

toward the discovery and characterization of new materials, and electron microscopy is expected to be readily available as a service tool. Many high-profile publications are produced in this manner. Equally remarkable, however, is the fact that many publications are no longer followed up, which is a strong indication that the underlying science was not as spectacular as initially thought. Sadly, electron microscopy is even used to prove a particular finding in one paper, and in another one it is used to disprove the very same fact with similar datasets. This conflicting practice is quite pronounced in the context of electron beam–sample interactions because visual inspections are tolerated as a substitute for measurements. The hope seems to be that the scientific truth will crystallize in time even if unsupported opinions would saturate the existing literature. Clearly, electron microscopic results are depicted in inconsistent ways, which point toward the existence of growing educational gaps.

Resultantly, any path forward is fiercely challenged in one manner or another. There is no doubt that incremental progress has served the community well in the past. However, progress in electron microscopy is not strictly incremental at all times as highlighted by the rapid rise of time-resolved electron microscopy [23, 24], the effective pursuit of cryo-microscopy [9], or the successes of environmental electron microscopy [15, 25]. Looking at these trends, one recognizes that these breakthroughs are now deeply embedded in chemical, biological, and environmental sciences. In addition, the control of beam–sample interactions has become a key element in these fields because of the necessity to make experiments more reproducible. The new approaches are attractive because they open a wealth of new opportunities but they also require the invention of more demanding experiments as the development of the "diffract-and-destroy" technique for X-rays has demonstrated [10]. Unfortunately, materials science hesitates to pursue techniques that address radiation control, and the trend remains strong to ignore any electron beam-induced structure alteration. This hesitation is somewhat unexpected because most interdisciplinary research calls for an integration of very diverse material components and for an exploitation of surface/interface properties [e.g., 26] all of which are radiation sensitive. Since calls for interdisciplinary materials research will only become louder with time, there is no doubt that further tool developments will occur that exploit the presence of beam–sample interactions. Luckily, there is the emerging opportunity that future needs can be met by building on the intrinsic strengths of elastic electron scattering and exploit dose fractionalization in "divide-and-conquer" experiments. They would conveniently complement the "diffract-and-destroy" approach, which exploits the strong inelastic interaction of X-rays with matter.

Consequently, one expects the deployment of significantly more complex experiments in materials science, or in other fields of scientific research, if it is not done there. They will not only require the fabrication of more complex material structures but also an even deeper understanding of electron optics, electron scattering, and quantitative contrast interpretation in conditions that embrace beam–sample interactions. In this respect, it seems counterproductive that knowledge about the details of electron scattering is only maintained in a rapidly declining number of dedicated institutions. Would it not be timely for the material science community to adapt the view that a quantitative image analysis must overwrite the growing culture of "visual inspections" and to acknowledge that beam–sample interactions are the most severe obstacle for progress in atomic resolution electron microscopy as shown in Fig. 1? A rich amount of new science is in plain view, but woven into the time evolution of material systems at different temperatures and pressures. Vacuum is only one of all possible environments and arguably the least relevant one. Principally, atom dynamics and functionality can now be explored in real time with atomic resolution and with single atom sensitivity if beam–sample interactions are seriously addressed and quantitative procedures for damage assessment are established. At least, it should become mandatory to provide electron doses and/or dose rates for any published high-resolution image; otherwise, the literature will be flooded with contradicting results of greatly different quality, which weakens the century-old standard of science to measure instead of claiming and invites a policy of "pick and choose."

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