Debye-Waller factors of copper, silver, and lead

C. K. Shepard* and J. G. Mullen

Purdue University, West Lafayette, Indiana 47907-1396

G. Schupp

University of Missouri Research Reactor, Columbia, Missouri 65211

(Received 11 June 1999)

Using very high intensity ($\sim$70 Ci) ^{183}Ta Mössbauer sources, we have measured the Debye-Waller factors (DWF's) for the (200), (400), and (600) Bragg reflections of three fcc metals (silver, copper, and lead) as a function of temperature from near 80 K to within about 100 K of their melting temperatures. Our reexamination of earlier measurements on these metals indicated problems with data analysis, and there are serious discrepancies between the present results and those reported earlier by Day, Mullen, and Shukla. We have corrected our data for the effects of thermal expansion, in a manner similar to our earlier paper [Phys. Rev. B **57**, 889 (1998)] on alkali halides and reinvestigated the anharmonic contributions to the DWF of these three metals. We have found significant Q^4 contributions to the DWF in both silver and copper, with m_4 values of $1.5(3) \times 10^{-13}$ Å^4/K^3 and $4.1(15) \times 10^{-14}$ Å^4/K^3, respectively.

I. INTRODUCTION

Measurements of the Debye-Waller Factor (DWF) in silver, copper, and lead were reported by Day, Mullen, and Shukla (DMS).[1,2] These measurements used very high intensity Mössbauer sources to eliminate many sources of systematic errors[4–15] found in earlier measurements of the DWF. However, this paper, as with many earlier works in this field, introduced an empirical parameter (m_3) to account for the thermal expansion of the crystals studied, rather than using the known coefficients of thermal expansion to directly correct scattering intensities. We have remeasured the elastic scattering from copper, silver, and lead, and reanalyzed the data using the direct measured expansion method, detailed in our earlier paper on alkali halide Debye-Waller factors.[3]

A closer examination of the recently reported results on copper, silver, and lead,[1] in preparation for a reanalysis, indicated calculational errors in the processing of data, resulting in the publication of an erratum,[2] which brought into question several points made in the original paper. It also led to some questions about the data which could not be resolved. Thermal expansion effects cause the Y values of the lower order reflections to appear to fall off very rapidly with increasing temperature, unless the data are corrected for the decrease in the number of scattering sites. (The Y values are rescaled elastic intensities, given by $Y = [(4\pi)^2/Q^2]\ln(I/I_0)$, where Q is the scattering wave vector, I is the elastic scattering intensity, and I_0 is the elastic scattering intensity at some reference temperature.) The data originally presented[1,2] had not been corrected for this effect, and the Y values do not show the expected behavior. The Y values also have less scatter in them than the properly calculated standard errors would indicate. We cannot reconstruct the actual uncertainties exactly from the available data. In particular, the uncertainties in the measurements of the integrated intensities are unknown, so our estimated errors are slightly smaller than the real statistical errors, but they are clearly an order of magnitude larger than the reported errors given in Ref. 1.

The surprising fact is that the scatter in the data is much smaller than expected for the correctly analyzed statistical errors. Some of the original data used in Day's thesis were not available to us so we could not confirm the Y values reported earlier by DMS.

Thus, we have repeated these measurements on the same three fcc metals to resolve these uncertainties and questions. We used the same crystals used by DMS, and our experiment was carried out with the same apparatus used in the earlier experiment and in our recently reported alkali halide studies.[3] We scattered 46.5-keV γ rays from a single crystal in reflection geometry, measured the integrated intensity of the Bragg peak, and measured the elastic scattering fraction using the Mössbauer technique. The data were then corrected for thermal expansion effects, using known thermal expansivity data,[17,18] and Y values were calculated as detailed in our earlier paper.[3] Before these corrections were made, the Y values at high temperatures for the (200) reflections were lowered relative to the (400) and (600) Y values, as would be expected from the change in number of scattering sites and in contrast to the earlier measurements reported on these crystals.

II. RESULTS AND DISCUSSION

After correcting for thermal expansion effects, we fitted our Y values to the function

$$Y = Y_H - (4\pi)^2[m_2 T^2 + Q^2 m_4 T^3], \qquad (1)$$

where Y_H is the harmonic term and m_2 and m_4 are the parameters for the anharmonic terms we are interested in. Figures 1–3 show the corrected Y values and the fitted curves. Our data are generally similar to that reported earlier by DMS, but the details are different. The present data show the expected scatter about the fitted curves. Also, the data for silver and copper show a very marked difference between the different reflections, showing a large Q^4 effect. While this separation between curves for different reflections was
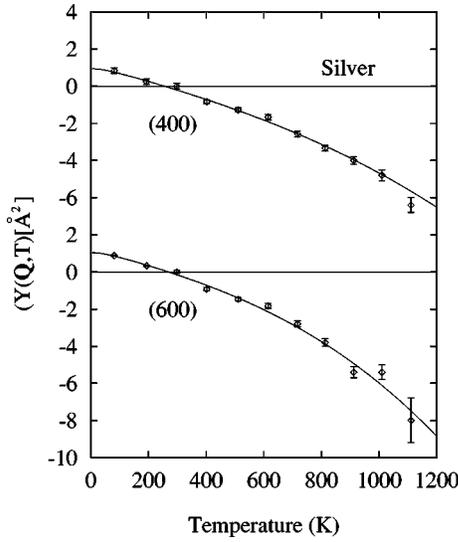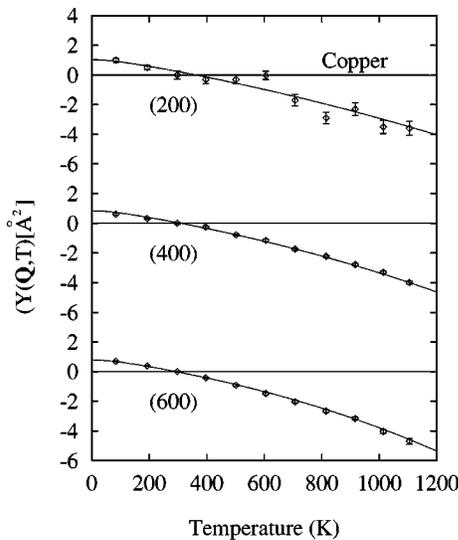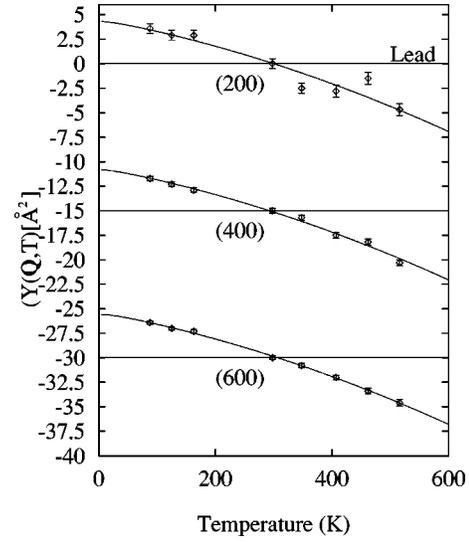

FIG. 1. A plot of $Y(\vec{Q},T)$ vs temperature for silver.

FIG. 3. A plot of $Y(\vec{Q},T)$ vs temperature for lead.

present in the earlier data, it was much smaller. The fitted parameters of interest are shown in Table I.

Our values for the Debye temperatures of these three metals are somewhat higher than those reported earlier. This is a result of our fitting the data for Θ_D and m_2 simultaneously while in the earlier DMS work Θ_D was determined by fitting only the low temperature data to a harmonic model. This method of fitting returns a lower Debye temperature than does a simultaneous fit using all the data, so our Debye temperatures are in good agreement with the earlier results as expected.

We cannot directly compare our m_2 values with that of DMS, because of our different methods of analysis. However, our values are of the same order of magnitude and show similar trends. For copper our value of 6.3(13) $\times 10^{-9}$ Å^2/K^2 is in good agreement with Martin and O'Connor value of 7.7(6)$\times 10^{-9}$ Å^2/K^2.[16]

It is in our determination of the m_4 parameter that the differences in our data and earlier work become evident. We find evidence for a substantial Q^4 term in both silver and

copper, much larger than reported by DMS and (in the case of copper) somewhat larger than Martin and O'Connor. (Note that our definition of m_4 differs from DMS's by a factor of 12, and the parameter reported by Martin and O'Connor is defined quite differently.) Our data in the case of lead is not as good, so we are unable to draw any conclusions about the presence of such a Q^4 contribution, though it could be quite large, as was noted earlier. Shukla's theoretical calculations reported by DMS suggested that the m_4 term should be four orders of magnitude smaller than the m_2 term. While our measured m_4 parameter is larger than that reported earlier, it remains quite small relative to the m_2 parameter. However, at high temperatures, the effect is easily observable.

III. CONCLUSIONS

Early Mössbauer measurements of DWFs were hindered by low source intensity, introducing systematic errors into the measurements. The later measurements of DMS using very high intensity sources did not have this problem, but, as with other earlier papers in this field, the initial analysis by DMS was flawed and did not properly account for thermal expansion. This data showed unexpected behavior, which our experiments, also using very high intensity sources, do not confirm. We find that it is necessary to directly correct the Y values for the thermal expansion of the sample, and that if this is not done the data cannot be properly fitted by including an additional empirical parameter. This is a claim

FIG. 2. A plot of $Y(\vec{Q},T)$ vs temperature for copper.

TABLE I. Debye-Waller factor parameters. The parenthetical quantity associated with each number is the error in the last figure of the measured quantity. When two digits are given in parenthesis, e.g., $\Theta_D = 340(12)$, we mean $\Theta_D = 340 \pm 12$.

Crystal	Θ_D (K)	m_2 (Å^2/K^2)	m_4 (Å^4/K^3)
Copper	340(12)	6.3(13)$\times 10^{-9}$	4.1(15)$\times 10^{-14}$
Silver	220(10)	2(3)$\times 10^{-9}$	1.5(3)$\times 10^{-13}$
Lead	99(11)	8(3)$\times 10^{-8}$	3(6)$\times 10^{-13}$

that we developed in analyzing our results on alkali halides, and it is an important departure from earlier reported data.

We properly analyzed our present data to determine the Debye-Waller factor parameters Θ_D, m_2, and m_4. These are summarized in Table I. The Debye temperatures are in reasonable agreement with earlier Mössbauer measurements, including those of DMS. Our m_2 values are to be preferred over those of DMS because of our better method of analysis, although our elimination of m_3 means that a direct comparison of the m_2 terms is of little meaning. Another very early measurement of m_2 for copper was made by Martin and O'Connor; our value is slightly lower than theirs, although they too did not properly correct for thermal expansion. We also find a significant quartic component to the DWF, except in the case of lead where our uncertainties are too large to permit us to draw any definitive conclusions. The presence of a nonzero m_4 is in agreement with the results of Martin and O'Connor[16] and the corrected results of DMS.[2] It should be noted that our values for m_4 are significantly larger than these earlier results. As the theoretical calculations reported by DMS suggest, our values for m_4 are roughly four to five orders of magnitude smaller than m_2, even though they are significantly larger than previously thought.

ACKNOWLEDGMENT

*Present address: Southwestern Illinois College, 2500 Carlyle Ave., Belleville, IL 62221.

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