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Change in KCl Lattice by Soft X-Rays*

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The lattice dimensions of powdered specimens of annealed and unannealed KCl were measured during irradiation by soft x-rays. One set of specimens was allowed to color during irradiation and another group was prevented from coloring by simultaneous white-light illumination. The following observations were made: There was an increase in lattice dimension during exposure for every specimen. No difference existed for specimens which were colored or not colored. Saturation in the change in lattice dimension occurred at a lower exposure for the unannealed specimens than for the annealed specimens. The total increase in lattice dimension was about $\Delta a/a=1\times10^{-5}$ for all specimens, compared with values given in the literature for maximum changes in length of approximately $\Delta l/l=20\times10^{-5}$. The difference indicates production of void volume, presumably Schottky defects. The failure to observe a difference between colored and uncolored specimens may be caused by a considerably larger production of Schottky defects than of color centers.

THE lattice dimensions of powdered specimens of KCl were measured during irradiation by soft x-rays. One group of measurements was made with light excluded from the KCl so that the crystals became colored, and another group was made with white-light illumination which prevented coloration. Analytical-grade KCl from Baker and Adamson was ground to produce a fine powder and three kinds of specimens were made from the powder: an unannealed specimen, and specimens annealed at about 500° and 600°C. The annealing was accomplished by keeping the powder at the elevated temperatures for about 16 hours and then cooling it to room temperature in about 24 hours.

The powdered KCl was packed lightly in a cavity in a metal block with no binder except diluted petroleum jelly, which also acted as a lubricant and tended to prevent changes in lattice dimension owing to pressure effects which have been reported earlier.[1] The flat specimens produced in this way were placed inside a constant-temperature jacket at about 25°C. The temperature of the air near the surface of the specimen was known to within 0.03°C and lattice dimensions were corrected to 25.00°C.

The lattice dimensions were calculated by determining the values, using Ni $K_{\alpha1}$ radiation, at diffraction angles of about 161 and 122 degrees and extrapolating to the value at 180 degrees, using the function proposed by Nelson and Riley.[2] Although this function was derived for a cylindrical specimen, analytical treatment shows that errors in the flat-specimen technique arising from such sources as incorrect positioning of the specimen or incorrect zero-angle adjustment may be greatly reduced by the extrapolation. The two diffraction peaks were read to the nearest 0.002 degree from a chart recording the rate of pulse generation in a Geiger counter detector as a function of angle. Corrections for refraction of the x-rays were made.[3] The two diffraction peaks were recorded in about 10 minutes and seven successive measurements were obtained from each specimen, the same source of radiation both coloring the crystals and producing the diffraction pattern. The radiation was from a nickel-target tube operating at 50 kvp and 8 ma.

Measurements of absolute intensity of the beam at the specimen were made with a calibrated ionization chamber described by Seemann.[4] To permit readings of relatively high intensity, a small lead diaphragm was placed over the window of the chamber. The effective wavelength of the incident radiation determined by using aluminum absorbers was about 1.58 A, not very different from 1.66 A, the characteristic radiation. The intensity at the center of the incident beam was 19.0 R/sec. This was converted to absolute intensity with the relationship of Seemann,[5] giving 160 ergs/cm² sec. If Harten's[6] value of 120 ev for the average energy of F-center formation in KCl at room temperature is applicable to our specimens, the rate of F-center production at the center of the surface may be estimated as

$$-(dI/dz)_{z=0}/120=\mu I_0/120=2.2\times10^{14}/\text{cm}^3\ \text{sec}.$$

The results of the measurements are shown in Fig. 1. Each point on the plot represents the average from

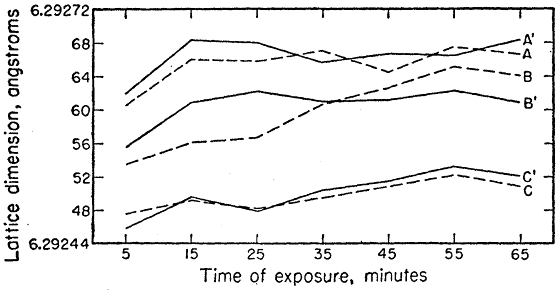

FIG. 1. Lattice dimension of KCl during x-ray exposure. A and A', unannealed specimens; colored by x-rays and prevented from coloring, respectively. B and B', annealed at 500°C; colored and not colored. C and C', annealed at 600°C; colored and not colored.

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about twenty separate specimens and has a standard error of 0.000015 A to 0.000020 A, as determined from the statistics. This error refers to the precision of the data, and the error in the absolute lattice dimension of pure KCl may be somewhat larger. The following conclusions appear from the figure: There is an increase in lattice dimension during exposure for every specimen. No significant difference exists between specimens which were colored and those which were prevented from coloring during irradiation. The lattice dimension of the unannealed specimens seems to rise more rapidly than the annealed specimens and then levels off. Since the difference in level of lattice dimension of the three sets of specimens may persist even at zero exposure, it may be attributed to changes produced during the annealing process or to certain systematic differences which we suspect, rather than to differences occurring during irradiation. Some additional measurements which were made following prolonged irradiation of the specimens for about 20 hours indicated that no significant change in lattice dimension occurred between 1 and 20 hours. The total increase in lattice dimensions is approximately $\Delta a/a=1\times10^{-5}$ for all specimens.

Since the x-ray beam was not of uniform intensity over the surface or in the depth of the specimen, the concentration of color centers and the change in lattice dimension were also not uniform. In addition, the various parts of the specimen are not weighted equally in a diffraction pattern. So it is of interest to determine how the measured change in lattice dimension is related to the value at the surface of the specimen in the most intense part of the beam. If it is assumed that the change in lattice dimension of an element in the specimen is proportional to the x-ray intensity incident on it, then

$$\Delta a(x,y,z)=KI_i(x,y,z)=KI_0(x,y)e^{-\mu_i z}.$$

The weight assigned to this element is proportional to the intensity in the reflected beam and is $I_r(x,y,z)\Delta x,\ \Delta y,\ \Delta z = I_{0\alpha}(x,y)\exp(-2\mu_\alpha z)\Delta x,\ \Delta y,\ \Delta z$. Averaging the contribution over the entire specimen gives the measured change in lattice dimension as

$$\langle\Delta a\rangle_{\text{Av}}=K\frac{\displaystyle\int\int\int I_0(x,y)I_{0\alpha}(x,y)\exp(-2\mu_\alpha z-\mu_i z)dxdydz}{\displaystyle\int\int\int I_{0\alpha}(x,y)\exp(-2\mu_\alpha z)dxdydz}.$$

Integration with respect to z in numerator and denominator gives the value $2\mu_\alpha/(2\mu_\alpha+\mu_i)$, which is very nearly $\frac{2}{3}$. Substituting this value and assuming that the total incident intensity $I_0(x,y)$ is proportional to the characteristic intensity, $I_{0\alpha}(x,y)$ gives

$$\langle\Delta a\rangle_{\text{Av}}=\frac{2K}{3}\frac{\displaystyle\int\int I_0^2(x,y)dxdy}{\displaystyle\int\int I_0(x,y)dxdy}.$$

These integrals were evaluated numerically from the map of intensity and gave a value in terms of the maximum intensity, such that

$$\langle\Delta a\rangle_{\text{Av}}\cong\tfrac{1}{2}KI_{\max}=\tfrac{1}{2}\Delta a_{\max}.$$

If the change in lattice dimension saturates at some exposure, the measured change will approach the saturation value. Thus, the change in lattice dimension measured in the diffraction experiment will correspond remarkably closely to the change produced in the most intensely irradiated portion of the specimen. This is a different situation from that in many other types of measurement, which weight the effect of all elements of the specimen equally, although the specimen is not saturated through the entire depth.

It is interesting to compare the maximum change in lattice dimension of KCl with related measurements discussed in the literature. Sakaguchi and Suita[7] determined that the increase in thickness of KCl saturated at a value, $\Delta l/l=5.7\times10^{-5}$. Estermann, Leivo, and Stern[8] found that the density decreased to a minimum such that $\Delta\rho/\rho=-7\times10^{-5}=-3\Delta l/l$. However, in both these cases, it was stated that the coloration decreased with depth such that the surface saturation values of $\Delta l/l$ were many times greater than those given above, possibly $\Delta l/l=20\times10^{-5}$. In any case, the surface saturation value for $\Delta l/l$ is many times greater than the saturation x-ray value of $\Delta a/a$. Then the density decrease and external expansion must be attributed primarily to an increase in void volume in the specimens, presumably Schottky defects, rather than to lattice expansion. If the saturation values for $\Delta l/l$ and $\Delta a/a$ are presumed to be about 20×10^{-5} and 1×10^{-5}, respectively, then the fraction of Schottky defects in the length of the specimen is almost 20×10^{-5}, or 6×10^{-4} in the volume. On this basis, the change of lattice dimension associated with formation of Schottky defects is $\Delta a=0.05a$ per defect. This is in a reasonable range to agree with the calculation of Mott and Littleton[9] that the nearest neighbors at a vacancy in NaCl are displaced outward by about $0.07a$.

It is rather puzzling that no difference was observed between the colored and uncolored specimens. A de-

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crease of about 0.15a in Δa per defect in the colored specimens was expected, owing to the reduction in Coulomb repulsion, which would occur on trapping an electron at a negative-ion vacancy. This estimate is suggested by the observation that a 15 percent decrease in lattice dimension occurs when a chloride ion is replaced by a fluoride ion in KCl. The observed result could occur in such a case only if the concentration of F-centers were many times smaller than the concentration of Schottky defects.

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Magnetic Susceptibility of Hafnium and Manganese

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The magnetic susceptibility of hafnium, which has been measured from 4.2°K to 1670°K, increases with increasing temperature above 77°K. At room temperature, the susceptibility is $(0.42\pm0.01)\times10^{-6}$ emu/g. The susceptibility of manganese between 77°K and room temperature shows a maximum at 125°K. This can be identified with antiferromagnetism by a correlation with neutron diffraction data. In the temperature region below 77°K the susceptibility increases again quite rapidly.

INTRODUCTION

THERE has been recent interest in the magnetic susceptibility of transition metals. On the basis of data recently obtained, Kriessman and Callen[1] have proposed a qualitative band theory interpretation of the temperature dependence of the susceptibility. We have extended this work by measuring the magnetic susceptibility of hafnium and manganese by the body-force method described in a previous paper.[2] The susceptibility of hafnium has not previously been measured while no data exist for manganese at low temperatures.

Manganese is of interest because Shull[3] has found evidence from neutron diffraction that it is antiferromagnetic with a Curie temperature at about 100°K. The only previous measurements on manganese in this temperature range are those of Serres.[4] They were limited to points at 80°K, 170°K, and room temperature, which gave some indication of a maximum in the susceptibility, an important characteristic of antiferromagnetism. It appeared that this feature needed further investigation to fix the exact location of the maximum value. No previous magnetic susceptibility data exist below 77°K, but it has been established by Goodman[5] using magnetic methods that manganese is not a superconductor down to 0.14°K. In all probability, Goodman's method would also have indicated a transition to ferromagnetism if it existed.

EXPERIMENTAL RESULTS

Hafnium

Our sample was obtained from H. K. Adenstedt of the Materials Laboratory, Air Materials Command, Wright-Patterson Air Force Base. Bommer[6] estimated from periodic table considerations that the susceptibility of hafnium should be about 0.5×10^{-6}. We find that the room-temperature value is $(0.42\pm0.01)\times10^{-6}$ and that the susceptibility increases regularly with temperature up to 1670°K, as shown in Fig. 1. The two upper curves (B and C) are from a series which one obtains from successive high-temperature runs. Curve A is the one finally reached, and, since it is reproducible and without field dependence, we assume it is the true behavior of the metal. The other curves evidently represent a ferromagnetic impurity whose effect slowly decreases on heat treatment. Measurements were also made at 77°K giving a value of 0.40

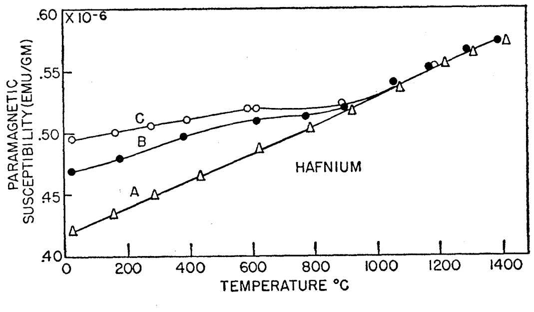

FIG. 1. Magnetic susceptibility of hafnium as a function of temperature. Upper curves (B and C) represent effects of ferromagnetic impurity.

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