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RAMAN SCATTERING BY OPTICAL MODES OF METALS*

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Raman scattering from the optical modes of the metals Be and AuAl₂ has been observed. The measurements were carried out using argon-ion laser excitation. One Raman line was observed for each of these metals. A frequency of 455 cm⁻¹ was obtained for Be and 266 cm⁻¹ for AuAl₂. The result for Be is compared with neutron scattering data.

We have observed Raman scattering from the optical modes of the metals Be and AuAl₂. Beryllium is of hcp structure with two atoms per unit cell. The space group for this lattice is D_{6h}^4 and there is one E_{2g} Raman active optical mode. Gold-aluminum has the CaF₂ structure and has one T_{2g} Raman active mode.

The Raman scattering was observed using argon-ion laser excitation. The sample was placed within the laser cavity with its polished face acting as a third cavity mirror. This type of sample configuration has been reported previously in application to Si and Ge. The AuAl₂ sample was a single crystal while the Be sample was a polycrystalline ingot with grain size of the order of several millimeters. The surface of both samples were mechanically polished.

One Raman line was observed for each of these materials. Figure 1 shows the Stokes line for Be with 4880-Å excitation. The Stokes component has also been observed for Be with 5145-Å excitation. Figure 2 shows the Stokes component for 4880-Å excitation which was obtained with the AuAl₂ sample. The anti-Stokes line for 4880 Å and the Stokes line for 5145 Å, respectively, were also observed for AuAl₂. It is evident from Figs. 1 and 2 that the Raman lines are superimposed on an appreciable background due to strong scattering of the exciting light from the

metal surface. This background is appreciable in comparison with the Raman lines because the Raman scattering is weak on account of the small scattering volume of the metals and because it is difficult to obtain a perfect polish on the metal surfaces. In Fig. 2 the background shown as a dashed line is subtracted from the recorder trace to give the Raman lines shown at the bottom of the figure. Table I gives the observed frequencies and linewidths at 300°K for these samples. The Raman intensity of Be was

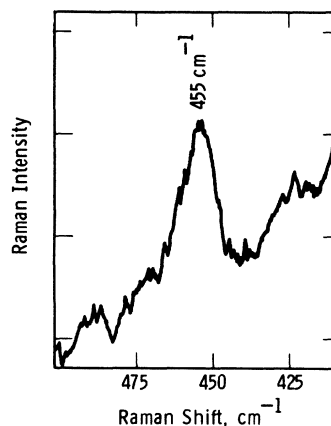


FIG. 1. Observed Raman line for Be metal; Stokes component for 4880-Å excitation. The instrumental resolution was 8 cm⁻¹, the time constant was 300 sec, and the scan rate was 1 cm⁻¹/min.

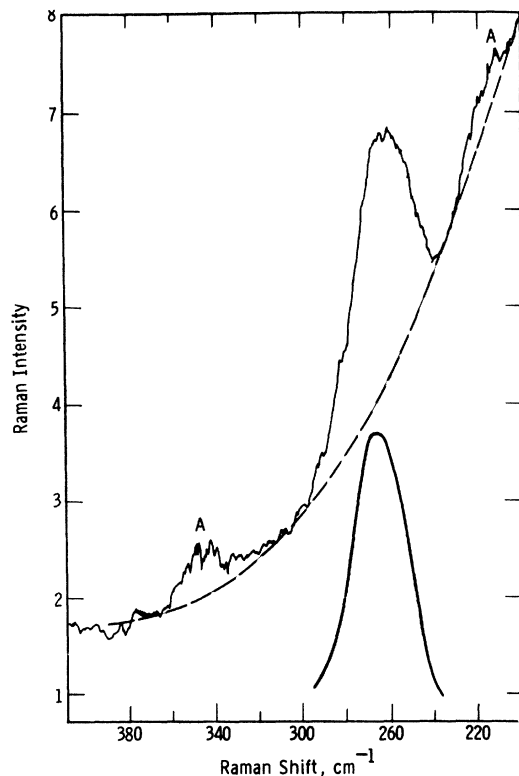


FIG. 2. Observed Raman line for AuAl_2 : Stokes component for 4880-\AA excitation. The small peaks marked *A* are argon discharge lines. The dashed curve represents background scattering which is subtracted from the recorder trace to give the Raman line at the bottom of the figure. The instrumental resolution was 12 cm^{-1} , the time constant was 60 sec, and the scan rate was $4\text{ cm}^{-1}/\text{min}$.

found to be about $\frac{1}{10}$ of that from Ge web,¹ under the same experimental conditions. The relative intensity of first-order Raman-scattered light for two different materials can be used to compare the values of the change in the electronic polarizability with lattice distortion for these two materials. Using Eq. (1) of Ref. 1 and our measured intensities for Be and Ge, we find that $a_{\text{Be}}/a_{\text{Ge}} \approx 0.16$, where a is the derivative of the polarizability with respect to lattice displacement. The value for the absorption coefficient

Table I. Raman frequencies and linewidths for Be and AuAl_2 at 300°K .

	ω (cm^{-1})	$\Delta\omega$ (cm^{-1})
Be	455	~ 16
AuAl_2	266	~ 28

for Be, which is approximately equal to that for Ge, was calculated from experimental optical constants.² Equation (1) of Ref. 1 does not take into account differences of reflectivity of the two materials; however, the reflectivities for Be and Ge are approximately the same. No detailed study has been carried out so far on the polarization properties of the scattering.

Inelastic neutron scattering, which has been carried out by Schmunk *et al.*,³ yields a value of 458 cm^{-1} for the Raman mode ($k=0$) of Be. This agrees quite well with our value of 455 cm^{-1} . In order to be positive that the line observed for AuAl_2 represented true Raman scattering, we compared the strength of the anti-Stokes component at 300°K with that at 77°K and found the expected reduction at low temperatures. It is of interest to compare the strength of the relevant force constants for the Raman mode of the metal AuAl_2 with those of the ionic solids of the same crystal structure. The quantity $M\omega^2$, where M is the mass of the negative ion and ω is the Raman frequency, should be proportional to the relevant force constant. The Raman frequencies of CaF_2 , BaF_2 , SrF_2 ,⁴ and UO_2 ⁵ are 322, 241, 286, and 445 cm^{-1} , respectively. The ratio of $M\omega^2$ for the ionic solids to that for AuAl_2 are as follows: CaF_2 , 1.03; BaF_2 , 0.58; SrF_2 , 0.81; and UO_2 , 1.66. For the CaF_2 structure, only the short-range part of the force constant is operative in the Raman mode because the equal and opposite motion of the two ions occupying the fluorine sites in the unit cell cancels out the long-range polarization. Therefore, the short-range force constants of the metal and these ionic solids do not differ by more than $\pm 60\%$. The Raman frequency observed for AuAl_2 can be compared with the frequency of 206 cm^{-1} derived from the Debye temperature of 297°K for this metal which was obtained from low-temperature heat-capacity measurements.⁶

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